Acid Deposition in the eastern Transvaal Highveld.

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ABSTRACT.

The Transvaal Highveld has one of the largest potentials for air pollution in South Africa. The area around Witbank and Middleburg in the eastern Transvaal Highveld, is highly industrialized with several coal-fired power stations, burning coal dumps and heavy industries. The pollution levels in this area have been the centre of much dispute in recent years, and yet little emphasis has been placed on the severity of atmospheric deposition despite the fact that acid deposition is a major world-wide environmental concern. This study focusses on the chemistry and severity of atmospheric depositions to the south and south-east of the Witbank-Middleburg Power and Industrial Complex. Bulk depositions were sampled at seven sites during the year August 1982 to August 1983 and rain samples covered five sites for four of the six months of the 1983/84 rainy season.

The atmospheric depositions sampled contained large amounts of sulphate, nitrate and chloride and exibited acidic tendencies. The volume weighted pH of the wet depositions varied between 4.23 and 4.39 and the lowest pH recorded was 3.72. The free acidity of the rain samples could be attributed to sulphate and nitrate ions. The depositions of these species were related to winds from the north-western to north-eastern sectors, implying that the pollutants originated from the direction of the Witbank-Middleburg Complex. There was little spatial variation in

the bulk deposition rates and the concentrations recorded in the rain water, implying the existence of a well mixed atmosphere over the eastern Transvaal Highveld. There was some evidence of higher sulphate depositions close to the source area and the increase in the acidity of the rain water with distance from the pollution sources was related to the spatial distribution of ammonium ions. The role played by dry deposition could be more important than that of wet deposition and more emphasis on this mechanism is suggested in future monitoring programs.

The magnitudes of depositions of the anthropogenically produced species measured in the eastern Transvaal Highveld are similar to those recorded in urban and industrial areas of Europe and North America. The estimated annual wet deposition of sulphate and hydrogen ions exceed the recommended limits for both ecologically sensitive and agricultural areas in North America. Should these thresholds be applicable to South African ecosystems, there is reason to be concerned about potential damage in the areas immediately down-wind of the Witbank-Middleburg Power and Industrial Complex.

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CHAPTER 1.

INTRODUCTION

to

ATMOSPHERIC DEPOSITION.

Thousands of tons of gaseous and particulate matter are discharged into the atmosphere daily during natural and anthropogenic activities. Eventually these return to the earth's surface and are a major source of acids, toxic metals and organics to terrestrial and aquatic ecosystems (Galloway, 1980).

The chemistry of atmospheric deposition varies from site to site. The anthropogenic components are usually alien to the receptor ecosystem and are likely to upset the ecological balance. Since these are often acidic in nature, their fallout is popularly known as acid deposition, and is currently recognised as one of the major world-wide environmental concerns (Wisniewski et al, 1982).

1.1 SOURCES OF ACID DEPOSITION PRECURSORS.

Acid deposition is attributed to strong mineral acids such as sulphuric, nitric and hydrochloric acid (Record, 1981). Table 1.1 lists acidic or potentially acidifying substances involved with the formation of acid deposition.

Table 1.1 : The major acidic or potentially acidifying substances associated with acid deposition.

Sulphur compounds and radicals:	
sulphur dioxide	(SO_2)
sulphur trioxide	(SO_3^-)
hydrogen sulphide	(H_2S)
dimethyl sulphide	($(CH_3)_2S$ or DMS)
dimethyl disulphide	($(CH_3)_2S_2$ or DMDS)
carbonyl sulphide	(COS)
sulphate	($SO_4^=$)
sulphuric acid	(H_2SO_4)
methyl mercaptan	(CH_3SH or MeSH)
Nitrogen compounds and radicals:	
nitric oxide	(NO)
dinitrogen oxide	(N_2O)
nitrogen dioxide	(NO_2)
nitrite	(NO_2^-)
nitrate	(NO_3^-)
nitric acid	(HNO_3)
ammonium ion	(NH_4^+)
ammonia	(NH_3)
Chlorine compounds and radicals:	
chloride	(Cl^-)
hydrochloric acid	(HCl)

1.1.1 Sulphur Compounds.

The natural sources of sulphur oxides include volcanoes, forest fires, seaspray containing sulphates from the oceans, organic compounds from bacterial decomposition of organic matter and reduction of sulphate in oxygen depleted waters and soils (Record, 1981; Murgatroyd, 1983). Crops such as alfalfa, corn, beans, tomatoes and peas, as well as trees such as pine and oak, have been shown to emit reduced sulphur gases (Aneja et al, 1984).

The combustion of coal and oil accounts for 75% of the total SOx emissions in the United States (Record, 1981). Ninety percent of these are believed to come from coal-fired power plants (Smith, 1980). The sulphur content of the coal burned is an important factor since nearly all the available sulphur is emitted either in the form of sulphur dioxide or sulphur trioxide (Bubenick et al, 1983).

Other important sources are heavy industry with those pertaining to primary metals, petroleum, chemical manufacturing and mineral products as the major contributors.

The natural-emission component of the sulphur cycle is sizable relative to anthropogenic sources on the global scale (Table 1.2). Man-made emissions tend to be more concentrated and therefore it is important to know the spatial distribution of these when considering the sources of acid deposition (Record, 1981; Bubenick et al, 1983).

Table 1.2 : Some estimates of the annual global emissions of Sulphur (Tg/yr) (after Record, 1981).

Source	Major Constituents	Estimates (Tg/yr)
Biological decay, land	H_2S	58 - 110
Biological decay, ocean	H_2S	30 - 170
Sea spray	$SO_4^=$	40 - 44
Volcanoes	SO_2, H_2S, $SO_4^=$	1 - 2
Rock weathering	$SO_4^=$	15 - 42
Industry and space heating	SO_2 and H_2S	40 - 70
Fertilizer to soil	$SO_4^=$	10 - 25

Tg: 10^{12} grams = 10^6 metric tons

1.1.2 Nitrogen compounds.

Nitrogen oxides (NOx) are emitted naturally during lightning discharges and by decomposition of nitrates in terrestrial and aquatic systems (Aneja et al, 1984). Stationary fuel combustion is the major producer of anthropogenic nitrogen. Transportation accounts for 43% of the total NOx emissions in the United States (Record, 1981), with two thirds of this due to gasoline combustion.

The contribution to atmospheric nitrogen by natural sources is uncertain. From the estimates presented in Table 1.3, it would seem, however, that more nitrogen is emitted naturally than by man.

1.1.3 Other compounds.

Ammonia, chlorides and particulate matter play important roles in the chemistry of acid deposition. Particulate matter are introduced into the atmosphere naturally (dust) and during human activities such as the combustion of coal (fly ash).

Natural dusts are composed of quartz, feldspar, carbonate minerals, dolomite, calcite and clay. These relatively large particles are usually deposited close to their origin. Some are hygroscopic and act as condensation nuclei during the formation of clouds but since most soil-derived particles are only partially soluble, little contribution to the chemistry of wet deposition is anticipated (Murgatroyd, 1983).

Table 1.3 : Estimates of the annual global emissions of Nitrogen compounds (Tg/yr) (after Record, 1981).

Sources	Estimates (Tg/yr)
Natural emissions from land to atmosphere	21 - 89
Natural emissions from land and sea to atmosphere	- 210
Tropospheric production by lightning	8 - 40
Stratospheric production from dinitrogen oxide	- 5
Atmospheric production from ammonia	3 - 8
Production during combustion	15 - 19
Other industrial production	30 - 36

Industrial particulate matter is much finer and is suspected to play an important role in gas-to-particle transformations during the long range transport of gaseous pollutants such as sulphur dioxide (Ananth et al, 1977). There is also limited evidence to suggest that fly ash neutralizes some of the acids (Likens et al, 1974; Shannon et al, 1974).

Ammonia neutralizes the acids in the atmosphere (Record, 1981; Bubenick et al, 1983) and is emitted naturally during the decay and decomposition of organic matter and anthropogenically during the manufacture of fertilizers, explosives, animal feed, nitric acid, acrylonitrile and amines. Natural emissions account for most of the atmospheric ammonia (Table 1.4).

The amount of chloride deposited from the atmosphere is small. The natural sources include salt spray from the oceans, volcanic activity and reactions in the upper atmosphere (Record, 1981). Anthropogenically produced chlorine and chlorides are emitted during the manufacturing, handling and liquification of chlorine gas and hydrochloric acid.

Most atmospheric hydrocarbons (HC) originate from the natural decomposition of vegetation. Vehicles are the primary source of man-made hydrocarbons. The combustion of fossil fuels and evaporation from petrol products are secondary sources (Oke, 1978). Despite being rather small compared to the natural releases, the anthropogenic production is very important because not only are some of the compounds potentially harmful to

Table 1.4 : Estimates of the annual global emissions of Ammonia (Tg/yr) (after Record, 1981).

Source	Estimates (Tg/yr)
Natural Emissions	
Biological decay	1054
Volatilized from land and sea	165 - 860 as N
Volatilized from land	113 - 244 as N
Forest fires	0.04
Anthropogenic Sources	
Coal combustion	4 - 12
Power generation	1.09
Industrial combustion	1.64
Fuel oil combustion	0.73
Natural gas combustion	0.02
Wood combustion	0.05

vegetation and humans, they are also highly reactive and can facilitate the formation of photochemical smog (Oke, 1978).

Goklany et al (1984) examined the trends in the emissions of particulate matter, sulphur oxides (SOx) and nitrogen oxides (NOx) in the United States between 1940 and 1980. The amount of particulates emitted into the atmosphere has decreased by about two-thirds, SOx emissions have increased by one third and NOx by two-fold. The decrease in particulates coupled with the increase in acid forming precursors may cause an increase in acid deposition in and around industrial centres. On the other hand, the decrease in manganese, iron and carbon emissions could result in a decrease in the catalyzed oxidation of SOx to sulphate by oxygen.

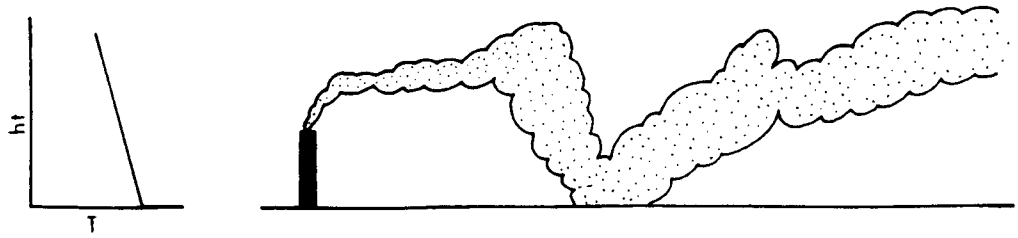
1.2 ATMOSPHERIC TRANSPORT AND DISPERSION OF AIR POLLUTANTS.

The first factor determining the degree of the atmospheric transport and dispersion of pollutants is the stack height (Oke, 1978). Chimney effluents are usually emitted at great temperatures with significant velocities and often contain large amounts of steam. The combination of temperature and emission velocity results in the plumes being unstable and buoyant. The height to which a plume rises before reaching

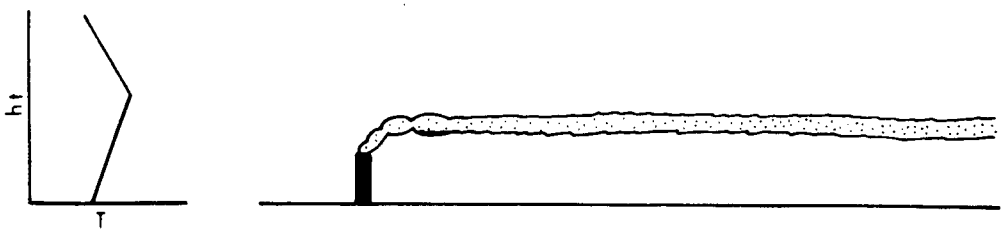
equilibrium with its environment is known as the effective emission height.

The severe pollution episodes experienced in Los Angeles and London during the 1950s led to the introduction of tall stacks. These were designed to emit effluent above the surface inversion, preventing the accumulation of ground-level pollutants near the source (Wilkens, 1954; Oke, 1978). Assuming that the plumes are emitted above the mixing layer and are not affected by aerodynamic downdraughts, the emissions may remain aloft for long periods of time and can be transported for hundreds of kilometers by the stronger winds at these altitudes (Fisher, 1981; Bubenick et al, 1983). The overall effects of using tall stacks are not clear, especially with respect to acid deposition. If the pollutants are emitted above the mixing layer, there is little doubt that long range transport occurs, that the pollutants are diluted and that the longer residence times for the gases enable complete gas-to-particle transformation (Fisher, 1981; Bubenick et al, 1983). It is generally believed that few plumes behave in this manner (Perhac, 1981).

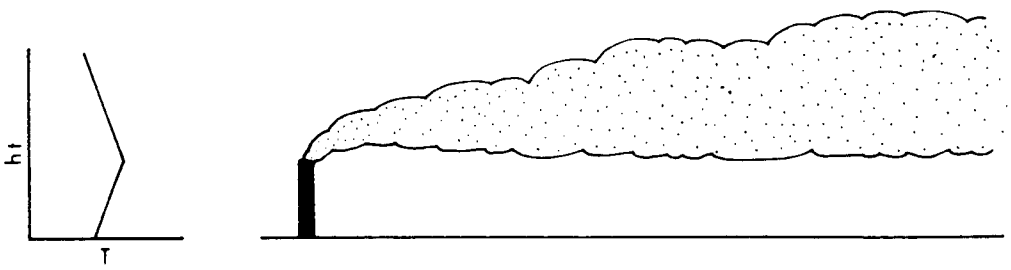
After its initial rise, the form, transport, dispersion and dilution of the plume is governed by the prevailing meteorological conditions. The vertical displacement of the pollutants is controlled by the stability conditions of the atmosphere and turbulence during the formation of clouds. Their diffusion and transport is determined by the prevailing wind (Oke, 1978; Isaac et al, 1983). If the sizes of the eddies are



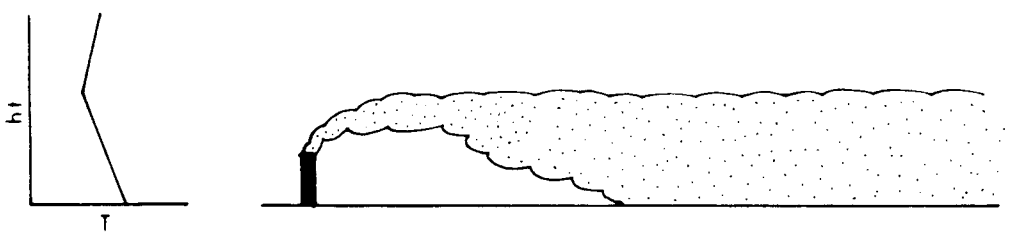
(i) Looping during unstable conditions.



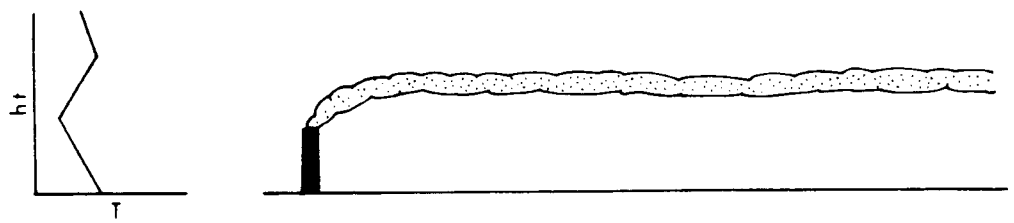
(ii) Trapped within a surface inversion.



(iii) Fanning above a surface inversion.



(iv) Fumigation in the unstable air capped by a subsidence inversion.



(v) Ribbon-like plume drifting in the stable subsidence inversion.

Figure 1.1 : The behaviour of the plumes during various atmospheric stability conditions.

smaller than the diameter of the plume, they will diffuse it, if larger, the pollution will be transported (Oke, 1978).

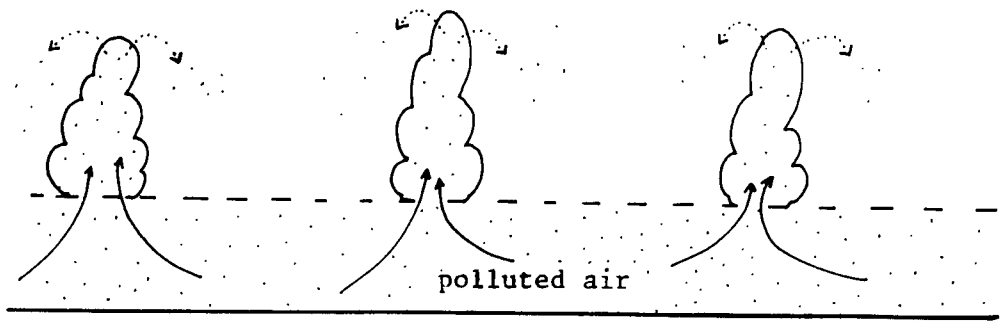
Free convection is an important means of diffusing material into a larger volume. The depth of the mixing layer sets an upper limit to the vertical dimensions of this volume. Thus the best conditions for the dispersion of pollutants usually occurs with strong instability and a deep mixed layer (Oke, 1978). This is characteristic of sunny day-time conditions especially in summer. The atmosphere is dominated by relatively large eddy structures which transport the plume up and down in a sinuous track (Figure 1.1(i)). This "looping" motion is capable of bringing the relatively undiluted plume in contact with the ground at quite short distances from the stack.

The worst conditions for dispersion occur when there is a temperature inversion and the boundary layer is stable. Turbulence is suppressed and the upward motion virtually eliminated (Oke, 1978). Surface inversions represent the most restrictive conditions (Venter et al, 1977). These occur at night as a result of radiative cooling of the earth's surface and are usually most intense just before sunrise, extending 50-100 m above the ground (Oke, 1978) although heights of up to 300 m have been recorded (Venter et al, 1977). Very calm conditions occur and the inversion lid acts as a cap, suppressing vertical mixing. Pollutants emitted into the inversion layer are trapped with very little transport and dispersion (Figure 1.1(ii)). Effluent emitted above the surface inversion are prevented from mixing

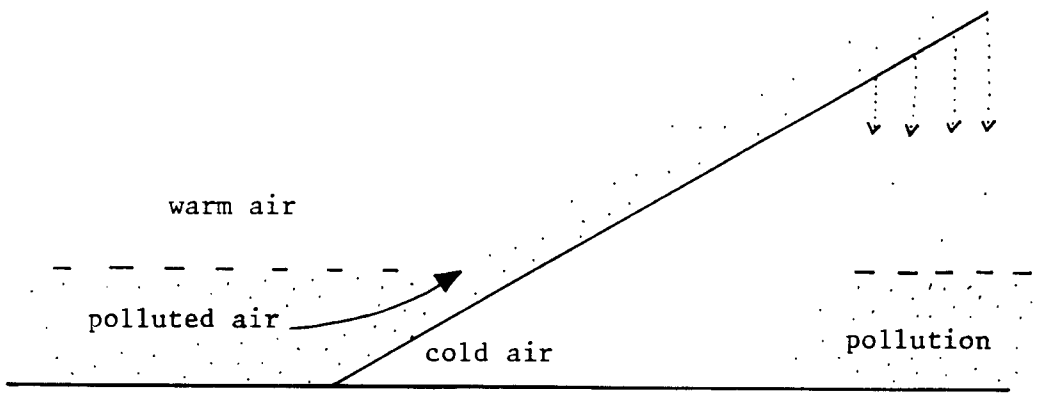
downwards by the stable layer beneath. The moderately unstable layer above the inversion allows the plume to fan upwards thereby enhancing dispersion (Oke, 1978) (Figure 1.1(iii)).

Subsidence inversions affect the regional air quality (Venter et al, 1977). These are caused by large stationary anticyclones and are usually found between 0.5-5 km above the ground. They are large scale phenomena which can persist for several days. The subsidence inversion forms an effective lid, capping the mixing layer and creating conditions of poor horizontal ventilation and limited vertical mixing. This stagnation develops into a murky mixed layer with a sharp upper boundary (Figure 1.1(iv)). Pollutants emitted into these inversions are trapped within a thin band of stable air and may be transported slowly for many kilometres with little or no dilution, before being deposited (Figure 1.1(v)). The lack of vertical turbulence keeps the plume thin but the erratic behaviour of the wind direction under such stable conditions allows the plume to meander across the sky (Oke, 1978).

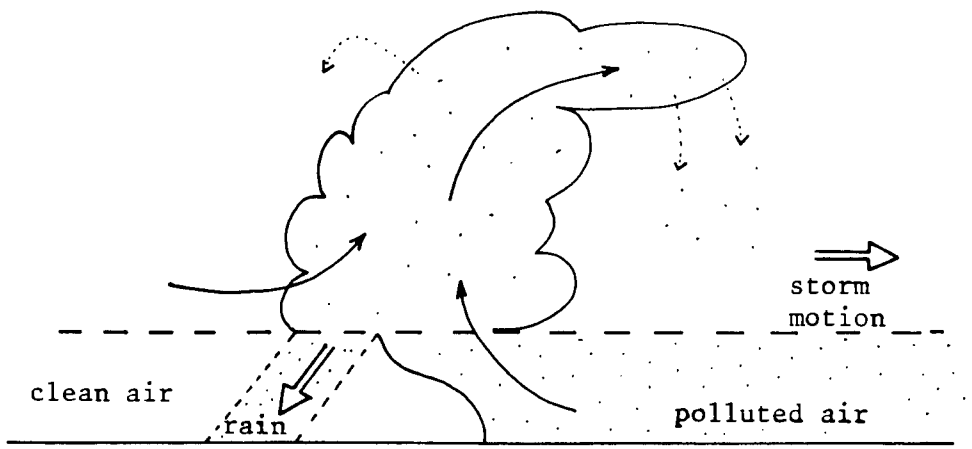
Pollutants can be carried aloft during cloud formation and dissipation (Isaac et al, 1983). Clouds created during weak convection, frontal and orographic activities disperse particulate matter vertically but it is during the strong convection of thunderstorms that transport to great heights occurs (Figure 1.2). The pollutants are transported vertically during unstable conditions. The winds are generally stronger and



(i) Vertical displacement during weak convection.



(ii) Warm frontal systems transporting pollutants vertically.



(iii) Transport to great heights during strong convection.

Figure 1.2: Cloud dynamics and the vertical transport of pollutants.

the potential for long range transport increases (Isaac et al, 1983).

Wind direction determines the path followed by the pollutants after their emission. This can result in multiple pollutant inputs due to the coincidental alignment of sources. In addition to the problem of cumulative loading this might result in the assemblage of a particularly reactive set of chemicals leading to the development of secondary pollutants downwind (Oke, 1978).

The nature of the surface wind is important when determining the transport of low level pollutants (Venter et al, 1977). Local circulatory systems such as land and sea breezes, city winds and mountain and valley breezes are not good pollution ventilators. These are closed circulations which exibit a diurnal change in flow and are characterized by low wind speeds. Thus there is little true air exchange. This can lead to a progressive increase in pollution loading with time (Oke, 1978).

The terrain of an area can also inhibit the dispersion and transport of pollutants. Turbulent eddies created in the lee of steep slopes or cliffs, valley inversions and tall buildings in urban complexes create aerodynamic traps.

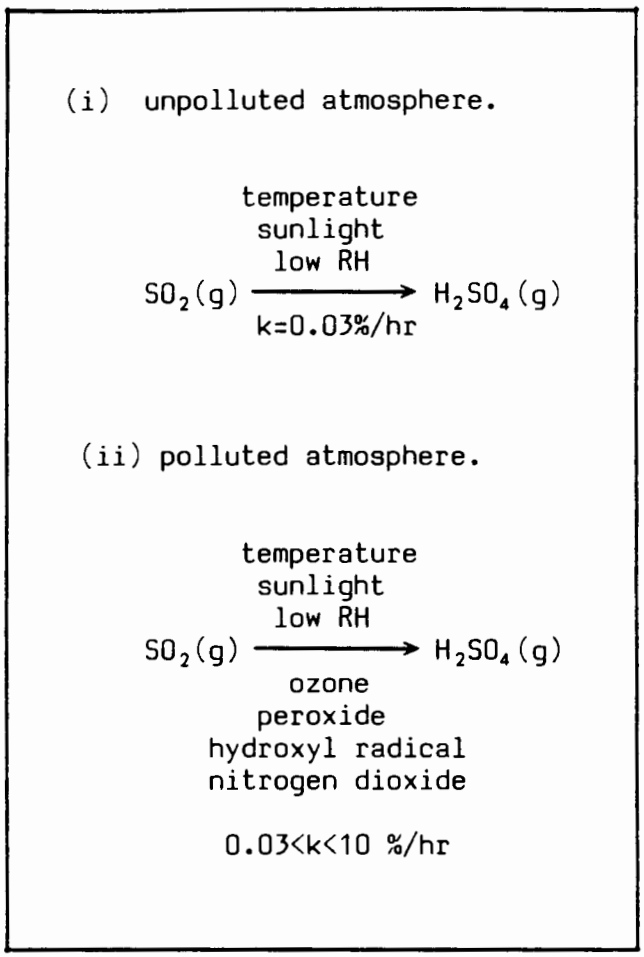


Figure 1.3 : Possible chemical pathways for the homogeneous oxidation of atmospheric sulphur dioxide (after Cox, 1974; Barnes, 1979 and Newman, 1981).

1.3 CHEMICAL TRANSFORMATION OF GASEOUS POLLUTANTS.

The harmful effects of acid deposition are associated with submicrometer sulphate and nitrate particles. The emissions of atmospheric sulphur and nitrogen are almost entirely in the form of gaseous oxides. Somehow these are converted to sulphate and nitrate particles prior to, during or after their deposition.

Little is understood about the chemistry of the atmosphere. The mechanisms and rates of the various reactions have usually been estimated under laboratory conditions or by the use of models (Record, 1981). Very little field work has been done, mainly due to the extreme difficulty in monitoring the chemistry of the atmosphere and the low concentrations of the reactant species.

1.3.1 Sulphur chemistry.

The atmospheric oxidation of sulphur dioxide can occur as a result of two types of reactions:

(i) Homogeneous reactions (Figure 1.3).

The photo-oxidation of sulphur dioxide to sulphuric acid vapour is a homogeneous reaction involving the gas phase only (Record, 1981; Oppenheimer, 1983). Direct photo-oxidation of sulphur dioxide in pure air is believed to be negligible and conversion rates of 0.03% per hour have been suggested (Cox, 1974). In polluted atmospheres this mechanism proceeds more

(i) catalysis by strong oxidants.

$$SO_2(g) \xrightarrow[\text{slow}]{pH} SO_2(aq) \xrightarrow[\begin{matrix}H_2O_2\ (g)\\ O_3\ (g)\\ OH^-\ (g)\\ NO_2\ (g)\end{matrix}]{} SO_4^{=}\ (aq/s)$$

(condensation nucleas or aerosol such as ammonium sulphate).

(ii) catalysis by transition metals.

$$SO_2(g) \xrightarrow[\text{slow}]{pH} SO_2(aq) \xrightarrow[Mn]{[SO_2]} SO_4^{=}(aq/s)$$

(condensation nucleas or aerosol such as ammonium sulphate).

(iii) surface catalyzed reactions.

$$SO_2(g) \xrightarrow[\text{fly-ash, soot particles, carbon particles}]{\text{reactivity of surface, low relative humidity}} SO_4^{=}(s)$$

Figure 1.4 : Possible chemical pathways for the heterogeneous oxidation of atmospheric sulphur dioxide.

rapidly after gas-phase collisions with strong oxidants such as hydrogen peroxide, ozone and the hydroxyl radical (Record, 1981).

The rate of homogeneous oxidation is believed to depend on the initial ratios of hydrocarbons to NOx, temperature, solar radiation, dew point and the absolute concentrations of the reactive pollutants (Record, 1981). A diurnal variation is usually observed with little or no oxidation at night and rates of 0.03-10% per hour at mid-day in summer (Barnes, 1979; Newman, 1981).

(ii) Heterogeneous reactions (Figure 1.4).

Heterogeneous reactions involve both the gaseous and liquid or solid phases. The first and most important step is the absorption of gaseous sulphur dioxide into the cloud or rain droplets. Due to the low solubility of sulphur dioxide, this is a slow process, possibly pH dependent and rate determining (Golomb et al, 1983).

Once dissolved the sulphur dioxide can be oxidized in the presence of strong oxidants or transition metals. Oxidants such as peroxide, the hydroxyl radical, ozone and nitrogen dioxide (Penkett et al, 1979a; Newman, 1981; Lee et al, 1983) and transition metals such as manganese (Penkett et al, 1979b) are considered the most important catalysts. Oxidation on fly ash,

carbon or soot particles may be significant near the source (Newman, 1981; Record, 1981; Dlugi et al, 1983; Oppenheimer, 1983), especially during episodes of low relative humidity (Mamane et al, 1979).

It is generally believed that the rate of the heterogeneous liquid-phase oxidation of sulphur dioxide in the atmosphere is much higher than the homogeneous gas-phase oxidation rate (Gillani et al, 1983). While the gas-phase reactions can proceed throughout the plume and continuously during the day, liquid-phase reactions only occur when and where the plume encounters the liquid phase. Thus in the long term and regional context, liquid-phase contributions to sulphate production can only be competitive if their local rates are substantially higher than those of the gas-phase reactions (Gillani et al, 1983).

Under relatively dry summertime conditions, the oxidation of sulphur dioxide in power plant plumes has been shown to be governed by homogeneous reactions (Gillani et al, 1981). However, in the presence of the low level convective clouds often associated with summertime conditions, the contribution to sulphate formation by homogeneous reactions may become less important (Gillani et al, 1983). The local conversion rates in clouds have been shown to reach an order of magnitude greater than the average for the plume (Gillani et al, 1983). If there

are cumulus clouds at the top of the mixing layer, a plume emitted into elevated stable layers may undergo a burst of sulphate formation (up to 10% per hour) during entrainment into the growing mixing layer in the late morning. There is also evidence to suggest that light rain may be even more conducive to sulphate formation, particularly in aged plumes (Gillani et al, 1983).

The relative roles played by the two types of reactions in transforming sulphur dioxide to sulphate have been estimated by Friend (1978). He attributes 10% of sulphate formation to homogeneous reactions and 90% to heterogeneous reactions. Gillani et al (1983) suggested that 40% of the oxidation of sulphur dioxide in power plant plumes in the mid-western United States (in summer) was due to liquid-phase heterogeneous reactions. Newman (1981) comments that the basis of choice is not definitive and that it is most likely that both mechanisms are at times dominant.

1.3.2 Nitrogen Chemistry.

The chemistry of nitrogen oxides in the atmosphere is complex and the details are not well understood. The conversion of NOx to nitrate takes place through a series of complicated reactions during which the participating nitrogen oxides switch back and forth between various stages of oxidation and eventually end up as nitrates (Record, 1981).

1.4 THE PROCESSES OF POLLUTANT REMOVAL.

The gases, aerosols and particles are removed from the atmosphere during the processes of wet and dry deposition.

1.4.1 Dry Deposition.

Dry deposition is a turbulent-transfer mechanism responsible for removing gases and particulate material from the atmosphere and depositing them onto the earth's surface without the intervention of precipitation (Oke, 1978; Garland, 1983). It involves a downward flux where the underlying surface acts as the pollutant sink. The dry deposition of particulates and gases is a function of height and depends on the aerosol dynamics, leaf surface chemistry, plant anatomy, land use and those meteorological parameters governing the turbulent wind distribution (Lewellen et al, 1983).

Although no particular method has gained universal acceptance, a variety of techniques are used to measure dry deposition (Wisniewski et al, 1982; Dasch, 1983). These fall into two basic categories. In the first category, the total accumulation of certain pollutants is estimated. Periods of time ranging from months to years are usually considered and short-term fluctuations cannot be identified. These methods could be used for routine monitoring but the effort required to maintain such a network is too great, considering the quality of the results obtained (Hicks, 1982).

The second category concerns flux parameterization. With successful parameterization, the vertical dry deposition fluxes can be calculated from the concentrations measured directly or computed in numerical models. This technique utilizes a series of methods such as box-budjet studies (Hicks, 1982), eddy correlation and accumulation methods (Hicks, 1982; Hicks et al, 1983a; Katen et al, 1983; Sievering, 1983; van Aalst, 1983; Wesely et al, 1983), variance correlation (Hicks et al, 1978), tracer methods (Sehmel, 1983) and surface accumulation (Lindberg et al, 1979, 1982; van Aalst, 1983). These methods usually require information on the pollution concentration profiles in both the vertical and horizontal axes, on the size distribution of particulates and on the micrometeorological status of the lower atmosphere. They are considered impractical for routine monitoring because the equipment is expensive and time consuming to operate, deposition and impaction are measured indirectly (although the disadvantages of this approach can be circumvented by monitoring under good fetch conditions) and most of the calculations require constants, many of which are crude estimates (van Aalst, 1983). The instruments used by parameterization techniques must have rapid response-times and be highly accurate and precise. For these reasons it is unlikely that these methods will be developed for routine application in the near future. At present they are only applicable to laboratory experiments aimed at understanding and parameterizing the depositional processes (Hicks et al, 1983b).

1.4.2 Wet Deposition.

The removal of pollutants during precipitation events is termed wet deposition. This phenomenon is popularly referred to as acid precipitation (rain) if its pH is less than 5.6 units. Recently, concern has been expressed at the use of this definition, mainly because the background pH of precipitation is largely undetermined and pH alone is insufficient to characterize the quality of precipitation (Mohnen, 1982). For these reasons, the term acid precipitation (rain) is used to describe that precipitation whose chemistry has been modified by anthropogenically produced pollutants, regardless of pH (Galloway, 1980; Reed, 1982).

Free acidity in precipitation may be caused by various proton donors such as strong acids (sulphuric and nitric acid), weak organic acids (acetic and formic acid) or metal oxides (aluminium and iron oxides) and therefore it is informative to devide the ionic components of precipitation into three categories: soil derived minerals such as calcium (Ca), magnesium (Mg), iron (Fe), silicate ions etc.; sea-salt derived ions such as sodium (Na) and chloride (Cl^-), with small amounts of sulphate ($SO_4^=$), potassium (K), magnesium and calcium; and atmospheric conversion products such as sulphate, nitrate (NO_3^-), ammonia (NH_4^+), chloride and hydrogen ions (Mohnen, 1982). Determining the role played by the atmospheric conversion products in modifying the precipitation chemistry and disturbing the ecological balance is the primary objective in acid precipitation research.

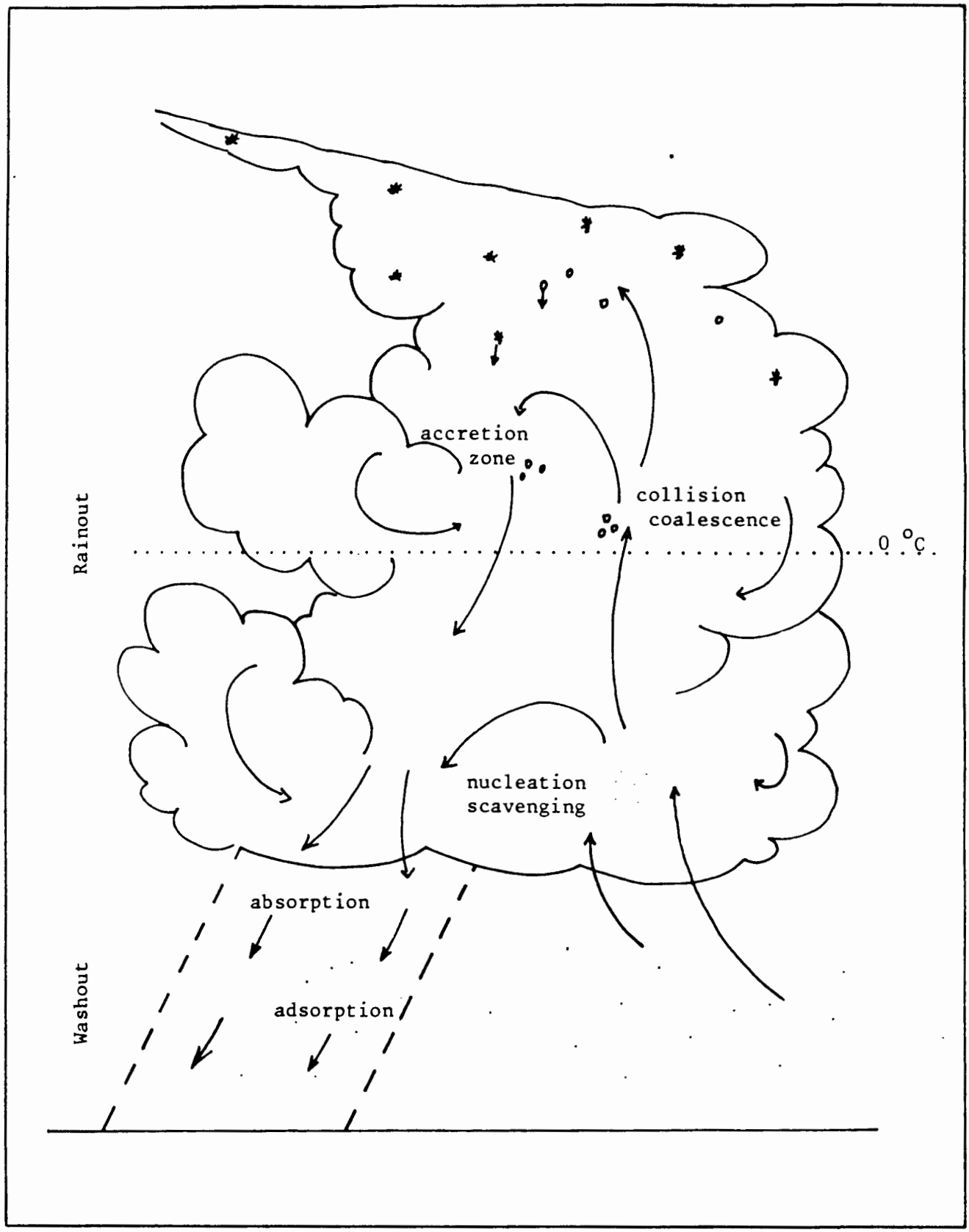


Figure 1.5 : The wet deposition mechanisms.

There are two mechanisms whereby pollutants are removed from the atmosphere during a precipitation event (Figure 1.5):

(i) rainout.

Aerosol particles may act as the nuclei for the formation of cloud droplets or they may be captured by existing drops or ice particles during nucleation scavenging (Hegg, 1983; Murray, 1983). Soluble gases are also absorbed by drops and are often rapidly oxidised during in-solution chemical reactions (Hegg, 1983).

The absorption of gases by cloud and rain droplets is dependant on the pH of the solution, drop size, droplet temperature, residence time within the cloud, ambient profiles of temperature and trace gas concentrations (Reda et al, 1982). Drops respond quickly to changes in the ambient concentrations of gases and when passing through elevated plumes, significant amounts can be absorbed, only to be desorbed later below the plume. This serves to transport gases from higher to lower elevations (Reda et al, 1982).

(ii) washout.

Washout, or below-cloud scavenging, is most effective for removing gases and large particles from the atmosphere (Altwicker, 1983). This mechanism is not considered efficient, since the lifetime of the raindrops is too short for appreciable

scavenging (Fisher, 1981; Hegg, 1983). Altwicker (1983) did, however, note that the washing out of gases and particulates could account for up to half of the free acidity, ammonia and nitrate present in Los Angeles rain. The role played by oxidation of sulphur dioxide to sulphate within the falling droplets over Los Angeles was also found to be significant.

The particles in the lower atmosphere are highly neutralized and some scientists feel that rain acidity can only be caused by preferential incorporation of acid forming species at cloud level during rainout (Harrison et al, 1983). This may involve direct incorporation of acid sulphates or of sulphur dioxide. Research has shown that the scavenging of sulphur dioxide during the rainout process, and its subsequent oxidation, may produce 50-75% of the sulphate in rain (Barrie et al, 1983). Sulphur dioxide therefore appears to be the major contributor to precipitation acidity (Reda et al, 1982). The absorption of sulphur dioxide depends on the range of drop sizes and therefore the intensity of the rain, the original pH of the solution, the ambient sulphur dioxide concentration and the absolute amount of sulphur dioxide already absorbed (Glover et al, 1979; Fisher, 1982).

Ammonia is very soluble because of its high gas-phase diffusivity and solubility. By decreasing the acidity of the

solution, the presence of ammonia may enhance further sulphur dioxide scavenging (Reda et al, 1982).

Gaseous nitric acid is also highly soluble in water and can be a significant contributor to the acidity of the precipitation (Overton et al, 1982; Reda et al, 1982). In the absence of peroxide, nitric acid is more effective than sulphur dioxide in acidifying rain. If hydrogen peroxide is present this is not the case, but the formation of sulphate from the absorbed sulphur dioxide is weakly dependant on the concentration of nitric acid (Overton et al, 1982).

Precipitation events are difficult to sample because of their random occurrence and the dilute samples are prone to contamination. The problems of sampling rain and snow for chemical analysis have been addressed by several authors (Berry et al, 1975; Galloway et al, 1976; Granat et al, 1976; Galloway et al, 1978, 1979; Hansen et al, 1982; Reed, 1982). Most errors seem to occur during sample collection, handling and storage.

The ideal precipitation collector should sample the event representatively relative to chemical composition (mg/l or μeq/l, where μeq/l = mg/l * charge on the ion/molecular weight of the ion * 1000) and ecosystem loading (mg/m^2 or μeq/m^2). The equipment must be free of any inherent sources of contamination. If the sampler is automated, a sensitive moisture sensor is recommended so that brief showers and the initial stages of the event can be sampled (Hansen et al, 1982). A co-located standard or recording rain gauge provides the necessary information on

rain volume, allowing the calculation of nett deposition during the storm (Vet, 1982).

The nature of the collecting surface has been shown to affect the chemical composition of the sample (Galloway et al, 1978; Peden et al, 1978). If the inorganic composition of the rain is of interest, Galloway et al (1978) recommend the use of plastic containers which have been pretreated with hydrochloric acid. Glass surfaces are potential ion exchangers and collection or storage of samples in glass could result in significant changes in the inorganic chemistry.

Precipitation samples are characterized by low ionic concentrations (~20mg/l) and biases introduced during handling and storage procedures can become the determining factors affecting reliable data aquisition and interpretation (Peden et al, 1978). The ionic stability of the sample is thought to be related to leaching, adsorption and consumation of species, oxidation of gases and particle-solute reactions taking place after the sample has been collected (Peden et al, 1978; Penkett et al, 1979b; Keene et al, 1983). Samples with a pH value less than 4.5 units exibit inherent preserving characteristics and if stored in a sealed container, in the dark and at 4 °C, the inorganic composition of most rain water samples will be preserved (Galloway et al, 1978). Because extraneous particulate matter is thought to play a role in disturbing the ionic integrity of a precipitation sample, Peden et al (1978) recommend pre-storage filtering.

The acidity of a sample need not be stable even if the sample is filtered and stored as recommended. The addition of chloroform has been shown to preserve pH and certain weak organic acids such as acetic and formic acid (Galloway et al, 1978, 1982).

Since the samples are ionically unstable, it is suggested that they be left in the field for a minimum length of time (Galloway et al, 1976; Skowron et al, 1979; Madsen, 1982; Vet, 1982; Keene et al, 1983; Böhm, 1984). In addition, an unnecessarily long sampling period increases the potential for sample contamination, loss of data, bias, physical changes and a poor time resolution of the data (Vet, 1982).

With modern technological advances in chromatography and spectrophotometry, there are few analytical difficulties. The measurement of the conductivity and free acidity (pH) of a precipitation sample can be problematic due to its low ionic strength (Galloway et al, 1979; Tyree, 1981; McQuaker et al, 1983). Galloway et al (1979) present a field method of determining the free acidity of a solution to within 0.02 pH units from which the hydrogen ion concentration can be calculated to within 5%. McQuaker et al (1983), however, have shown that the accurate determination of precipitation pH requires careful calibration procedures under controlled laboratory conditions. They believe that these conditions cannot be recreated in the field and therefore on-site measurements of pH are unlikely to be within 0.1-0.2 pH units.

The measurement of various other parameters such as wind speed and direction (at ground level and in the upper air), rain intensity and air quality (at ground level and in the upper air) provide useful data for determining the origin of the chemical species in the precipitation (Vet, 1982).

Until recently, wet deposition was considered to be the chief mechanism for removing pollutants from the atmosphere and re-depositing them on the surface of the earth (Record, 1981). Ecologically, the detrimental effects of acid precipitation may be more serious in that large amounts of alien chemicals are deposited over a short period of time. However the continuous nature of dry deposition makes it potentially more important (Record, 1981; Lindberg et al, 1983). Estimates of the ratio of wet to dry deposition have indicated that this may be the case and it is generally recommended that more emphasis be placed on dry deposition in the future (Record, 1981).

1.4.3 Bulk Deposition.

Atmospheric fallout comprises of wet and dry deposition components. These are collectively called bulk deposition. In some long term ecological studies it is more important to know the nature and amounts of the bulk than the contribution by wet or dry depositions.

Bulk depositions have been traditionally measured using a cylindrical vessel facing up to receive descending particles and gases. The bucket is usually constructed of polyethylene or polypropylene and is often partially filled with deionized water (Strauss, 1978; Hicks, 1982). These deposit gauges need to be exposed to the atmosphere for prolonged periods of time so that sufficient material can be collected for analysis (Strauss, 1978).

Petri dishes, flat plates and shallow pans are in principal similar to the traditional deposit gauge. Sometimes discs of Whatman 41 cellulose filter paper are attached to the inside surface of the petri dishes.

These methods are widely criticized because short-term fluctuations in the deposition rates cannot be detected, there is poor particle size discrimination, the data are in the form of point measurements, the relationships between deposition to natural and surrogate surfaces are not understood, the data are difficult to interpret and the accuracy is debatable. Deposited particles may be modified by their exposure to trace gases in the air including water vapour and solar radiation (Hicks, 1982).

The hypothesis that stagnant air creates a "lid" preventing the deposition of small particles to deep containers is dispelled by Volchok (1980). Dasch (1983) suggests the use of flat plates or rimmed petri dishes with filters, should the researcher be concerned about this.

The efficiency with which particles are retained in the collection containers has been extensively investigated (Clough, 1973). The use of fibrous filters, inert sticky films or deionized water to trap the particles and prevent re-entrainment is recommended.

It is generally recognised that surrogate surfaces do not simulate the microscale roughness features of natural surfaces (Hicks, 1982). The results of a study by Sickles et al (1983) suggest that the apparent deposition to surrogate surfaces was not representative of that to living Liqustrum leaves. In a similar experiment Lindberg et al (1983) concluded that the deposition fluxes to inert, surrogate surfaces were comparable to or exceeded those estimated for foliage within a forest canopy. They also observed that the size and morphology of the particles deposited on each surface was similar. Dasch (1983) tested various surrogate surfaces for reproducibility, surface roughness effects, gaseous absorption and the effects of placing the collection surface facing upwards or downwards. The results indicated that there were a range of collection efficiencies between surrogate surfaces as there undoubtably are for natural surfaces. Metals, nitrate and sulphate showed similar depositions regardless of surface, gravitational settling was the most important process of deposition and the collectors maintained consistent trends between one another. Dasch therefore came to the conclusion that it was possible to estimate deposition to natural surfaces using surrogate collectors.

Bulk deposition gauges do not measure the deposition of trace gases or the small particles which are deposited by impaction and interception (Hicks, 1982). It is suspected that the values recorded for sodium, chloride, ammonium ions and sulphate are on the high side due to hygroscopic growth over smooth wet surfaces (Garland, 1983).

Finally, it is recommended to monitor wet and dry depositions separately since the chemistry of precipitation can be completely masked by the presence of dry depositions (Galloway et al, 1978; Hansen et al, 1982). However, the equipment required to measure wet and dry depositions are often too complicated and expensive to operate on a routine basis.

Despite the numerous criticisms and limitations of these methods, they have often been used in the past (Strauss, 1978). If the networks are carefully designed, inert surfaces do provide useful estimates of the deposition of large particles in particular. Actual measurements are obtained, sufficient sample is collected for complete chemical speciation and the simplicity of the methods permit spatial replication and routine monitoring with low running costs (Hicks, 1982; Lindberg et al, 1983).

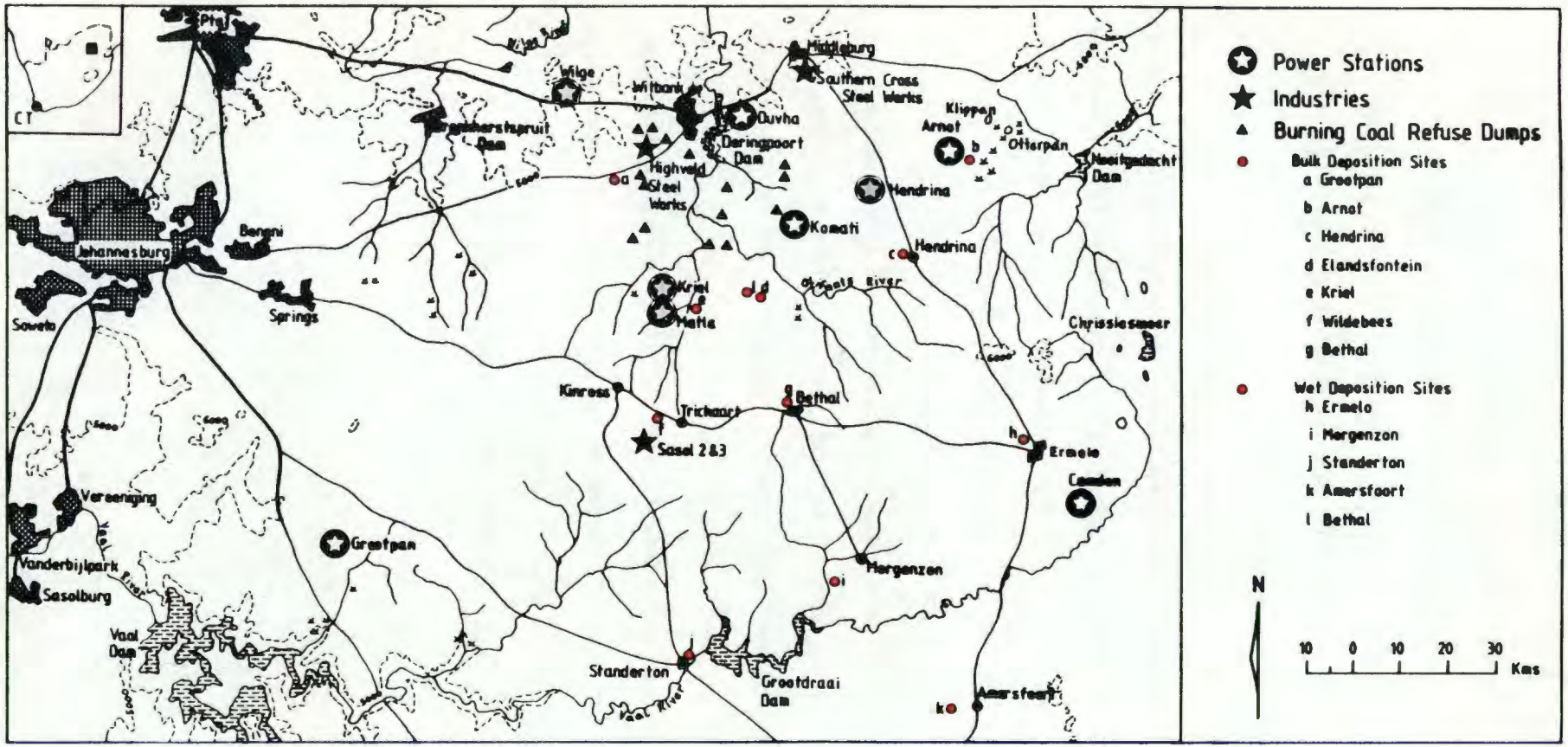


Figure 1.6: The locations of the pollution sources and the atmospheric deposition monitoring sites in the eastern Transvaal Highveld.

1.5 ATMOSPHERIC DEPOSITION IN SOUTH AFRICA.

The air pollution potential of an area can be determined by considering those meteorological conditions conducive to the accumulation of atmospheric pollutants. It is a function of vertical mixing and horizontal dispersion. An analysis of mesoscale variations in afternoon mixing depth and mean transport wind speed across South Africa indicated the interior northern, north-western and western regions as having the highest air pollution potential (Diab, 1977). Venter et al (1977) suggested the Transvaal Highveld as being the most likely area for the development of a serious air pollution problem. They also reasoned that the winter period experienced the most severe conditions and that dry deposition was the dominant removal mechanism of these accumulated pollutants.

The eastern Transvaal Highveld is highly industrialized especially around the Witbank-Middleburg area. Seven mine-mouth coal-fired power stations (total generating capacity 14000 MW and burning 135000 tons of coal, with an average 1.1% Sulphur content, per day) together with numerous smoldering coal dumps and several heavy and light industries are concentrated in this region (Figure 1.6) (Annegarn et al, 1983). The air pollution levels in this area have been the centre of much dispute in recent years, and yet little emphasis has been placed on the nature and severity of atmospheric depositions, despite the fact

that acid deposition is considered one of the major world-wide ecological concerns.

Acid deposition is attributed to anthropogenic sulphur, nitrogen and chlorine. These acid forming pollutants are emitted to the atmosphere during the combustion of fossil fuels, metal fluxing in the iron and steel industry and the manufacture of chemicals. All of these activities occur in the Witbank-Middleburg Power and Industrial Complex and therefore acid deposition could be anticipated downwind of this large pollution source-area.

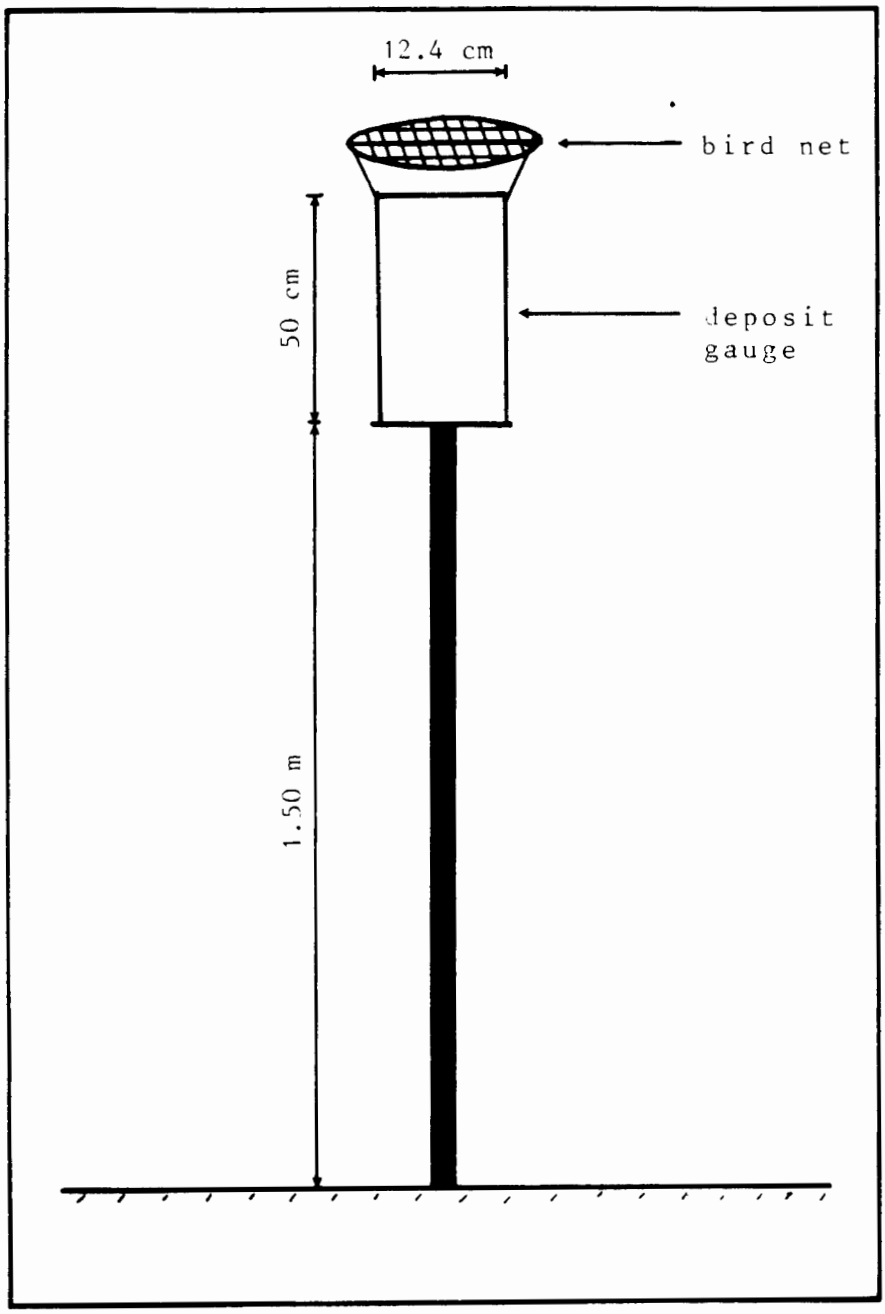


Figure 2.1: A field site showing the deposit gauge and bird net mounted on a pole.

CHAPTER 2.

BULK DEPOSITIONS in the eastern TRANSVAAL HIGHVELD.

The bulk deposition of acidic materials in the eastern Transvaal Highveld was studied from August 1982 to August 1983. The influence of local sources such as power stations and urbanization as well as the nature and severity of the depositions were considered. The data were collected to provide preliminary information on the status of acidic depositions in this area.

2.1 METHODOLOGY.

The samples were collected using cylindrical vessels partially filled with deionized water (Figure 2.1). These resembled the standard deposit gauges described by Strauss (1978). The evaporation of deionized water during the dry winter months was offset by increasing the length of the gauge by 16.5 cm and therefore its volume by 2 litres. The extra deionized water was sufficient to prevent complete drying out during exposure.

Table 2.1 : The physical characteristics of the seven bulk deposition sites.

Characteristics	Rural		Small Urban Centres		Industrial towns		Rural/Indust
	Grootpan	Elandsftn	Bethal	Hendrina	Arnot	Kriel	Wildebees
Wind Data	Y	Y	Y	N	Y	Y	Y
Access Road	grass covered track	grass covered track	tarred road	grass covered track	tar road	dust road	tarred road
Local Influences: Industry	N	N	N	N	coal-fired power plant 5 km to north-west	two coal-fired power plants 15 to 20 km to west	Sasol 2 & 3 less than 20 km to south-west
Towns/Cities	Oogies less than 20 km to south-west	Bethal less than 30 km to south	within town limits	within town limits	within town limits	within town limits	small urban centres 15-20 km to east and south-east
Road/Rail	tarred road 500 m, rail 1 km	dust road 200 m, tarred road 5 km	tarred road 50 m, dust road 200 m	dust road 50 m, tarred road 500 m	tarred roads 50 m	tarred road 500 m	tarred road 1 km, rail 1 km
Landuse	fallow field	fallow field	urban	urban	urban	urban and maize farming	urban and maize farming
Ground cover	cut veld grass	short veld grass	cut grass	veld grass	cut grass	veld grass	cut veld grass
Overhead Obstacles	N	radio mast telephone wires	N	N	N	N	N

Despite the criticisms levelled at collecting wet and dry depositions together as bulk samples and the short comings of the deposit gauge technique, this procedure was used because there were insufficient funds to monitor wet and dry depositions separately on a spatial scale and the limitations on laboratory facilities prevented the collection of too many samples.

The sites were chosen within the source area (Figure 1.6). They were placed in disused, open fields with an aged grass cover, away from local sources, overhead wires, trees and other vertical structures taller than 2.0 m, roads and railway lines. Where possible, the adjacent fields were also dormant. The access roads were usually grassed and were rarely used (Table 2.1). Two of the sites were specifically placed within small urban settlements (Bethal and Hendrina), Arnot and Kriel were located beside large power stations, Wildebees was near to the Sasol 2&3 complex at Secunda and Elandsfontein and Grootpan were rural sites. Surface wind direction was available at each site except Hendrina.

2.1.1 Experimental Techniques.

The deposit gauges were constructed from PVC plastic and positioned 2.0 m above the ground. Deionized water with a conductivity value of between 0.5 and 2.0 $\mu S/cm^2$ was used as a trapping agent to prevent re-entrainment of the particles deposited. Ideally the gauges were exposed for fourteen days but this was not always possible (Table 2.2).

Table 2.2 : The dates and lengths of the exposure intervals for the bulk deposition gauges.

Exposure Period	Interval	Exposure days
1	23 Aug 82 - 06 Sep 82	14
2	06 Sep 82 - 23 Sep 82	17
3	23 Sep 82 - 07 Oct 82	14
4	07 Oct 82 - 22 Oct 82	15
5	22 Oct 82 - 03 Nov 82	12
6	03 Nov 82 - 22 Nov 82	19
7	22 Nov 82 - 06 Dec 82	14
8	06 Dec 82 - 21 Dec 82	15
9	21 Dec 82 - 04 Jan 83	14
10	04 Jan 83 - 18 Jan 83	14
11	18 Jan 83 - 02 Feb 83	15
12	02 Feb 83 - 15 Feb 83	13
13	15 Feb 83 - 01 Mar 83	14
14	01 Mar 83 - 16 Mar 83	15
15	16 Mar 83 - 31 Mar 83	15
16	31 Mar 83 - 14 Apr 83	14
17	14 Apr 83 - 29 Apr 83	15
18	29 Apr 83 - 13 May 83	14
19	13 May 83 - 10 Jun 83	28
20	10 Jun 83 - 24 Jun 83	15
21	24 Jun 83 - 13 Jul 83	18
22	13 Jul 83 - 28 Jul 83	15
23	28 Jul 83 - 10 Aug 83	13

The canisters were washed copiously with hot deionized water. The surfaces were gently cleaned with a carefully prepared brush used only for this purpose. The conductivity of the final rinse water was checked against that of the hot deionized water used. The canisters were considered clean when these were equal. Each deposit gauge required about ten rinses before this criterium was satisfied. They were then capped using tightly fitting lids which were washed using the same procedure described above. To ensure the canisters remained clean during transport, the lids were sealed with tape.

In the field, the exposed gauge was taken from the pole and the bird-net gently removed. The lid of the clean canister was used to cover the exposed gauge. If any bird droppings were present on the net, these were carefully washed off using deionized water. The clean canister was rinsed twice with deionized water before being shaken dry. All the inside surfaces were wetted during this process. About six litres of the same deionized water were then added. The net was secured to the top of the clean canister which was then placed on the pole.

The exposed canisters were taken to the laboratory the following morning. The samples were first filtered before detailed analysis (Table 2.3).

2.1.2 Data Presentation.

The rates of deposition ($mg/m^2/day$) are presented in the form of graphs. Spatial variations are illustrated using

Table 2.3 : The analytical techniques, with their detection limits for solutions of low ionic strength, used in determining the chemical compositions of the bulk and wet deposition samples.

Element	Techniques	Detection limits
Fluoride	Standard ion chromatography /DIONEX 2120I IC	0.04 mg/l
Acetate	"	0.04 mg/l
Formate	"	0.04 mg/l
Chloride	"	0.04 mg/l
Nitrate	"	0.03 mg/l
Sulphate	"	0.02 mg/l
Sodium	"	0.05 mg/l
Ammonium ions	"	0.05 mg/l
Potassium	"	0.12 mg/l
Calcium	Atomic absorption spectrometry using standard methods.	0.01 mg/l
Magnesium	"	0.001 mg/l
Aluminium	Atomic absorption spectrometry using std carbon rod techniques	0.001 mg/l
Iron	"	0.0004 mg/l
Manganese	"	0.0001 mg/l
pH	pH meter /Radiometer-Copenhagen PHM83 with combined glass calomel electrode using a standard two point calibration with buffers 4.01 and 7.00. The pH reading was corrected for temperature.	0.01 pH units

isoline maps of annual deposition (kg/Ha/yr) and wind roses showing the percentage occurrence of direction.

The variations in deposition across space and time were considered statistically using 2X2 ANOVA tests without replication. Missing data were estimated to facilitate the analysis. If the deposition rate was known for the periods before and after the period missing data, these were estimated from the average of the two known values. If more than one missing point occurred, the data were estimated using the iterative procedure described by Steel et al (1960).

The results of the ANOVA tests were further investigated using the Student-Newman-Keuls procedure, a stepwise method using the range as the statistic to measure differences among means. The sites or periods causing the variation detected by the ANOVA tests were then identified (Sokal et al, 1969).

The role played by the wind in determining the amount and nature of bulk depositions was considered using Pearson's Moment Correlation Coefficients (Sokal et al, 1960).

Table 2.4 : The correlations between the frequency of occurrence of hourly mean wind-direction during the exposure interval and the amount of bulk deposition recorded, as determined by the Pearson's moment correlation coefficients (***, $p<0.01$; **, $p<0.05$). Where relevant, negative correlations are noted (- ve). Non-significant correlations are not included.

Site	Element	Wind Direction	Significance
Grootpan			
Elandsftn	Fluoride	ESE	***
		E	**
	Chloride	NE	**
		NW	** (- ve)
		SSW	** (- ve)
	Nitrate	NE	**
		ENE	**
		SW	** (- ve)
		WSW	** (- ve)
	Sulphate	ESE	**
		NW	** (- ve)
	Calcium	NNE	**
	Aluminium	NE	**
		ENE	**
		SW	** (- ve)
		WSW	** (- ve)
	Iron	ESE	**
	Manganese	ESE	**
		SE	**
		WSW	** (- ve)
		NW	** (- ve)
Bethal	Chloride	S	** (- ve)
	Nitrate	SSE	** (- ve)
		SSW	** (- ve)
	Calcium	SSE	** (- ve)
		S	** (- ve)
	Aluminium	SSW	*** (- ve)
		SW	** (- ve)
		WSW	** (- ve)
	Iron	SSW	** (- ve)
	Manganese	SW	** (- ve)
Hendrina			
Arnot	Chloride	NW	**
		SW	** (- ve)
	Nitrate	NE	**
	Sulphate	NW	**
		S	** (- ve)
	Potassium	ENE	**
		S	** (- ve)
		SW	** (- ve)
	Calcium	ENE	***
	Magnesium	ENE	**
		SW	** (- ve)
	Iron	NW	**
		SW	** (- ve)
	Manganese	SE	**
		SW	** (- ve)
		WSW	** (- ve)
		NW	** (- ve)
Kriel	Calcium	SE	** (- ve)
		SSE	** (- ve)
		S	** (- ve)
		SSW	** (- ve)
		SW	** (- ve)
	Magnesium	E	** (- ve)
Wildebees	Nitrate	NW	**
	Sulphate	ENE	**
	Aluminium	ENE	**
		SW	** (- ve)
		WSW	** (- ve)
	Iron	ENE	**
		SW	** (- ve)
	Manganese	ENE	**
		SW	** (- ve)

2.2 RESULTS.

2.2.1 Grootpan.

The Grootpan site was located near the town of Oogies, to the west of the major pollutant sources (Figure 1.6). Originally it was chosen to monitor background levels.

Very little fluoride, aluminium, iron and manganese were deposited at this site. The deposition rates of sulphate, calcium and magnesium were reasonably constant throughout the study period. Nitrate and iron were deposited erratically and the deposition rates of chloride and manganese increased noticably in summer (Appendix 2: Figures 2.2-2.12).

Wind direction was not correlated to the deposition rates of any element.

2.2.2 Elandsfontein.

The bulk deposition gauge was located on the highest hillock in the area around Bethal. Six of the power stations could be seen from this site (Figure 1.6).

Very little potassium was deposited at this site. Sporadic depositions of fluoride were monitored. Sodium and nitrate were deposited in quite large quantities but erratically whereas the deposition rates of sulphate, chloride and calcium remained reasonably constant throughout the study period. An increase in the deposition of aluminium occurred during the summer months (Appendix 2: Figures 2.2-2.12).

Deposition rates of chloride, nitrate, calcium and aluminium were positively correlated with winds from the north-eastern sectors and that for fluoride, sulphate, iron and manganese with south-easterly winds. Winds from the south to north western sectors were negatively correlated to depositions of chloride, nitrate, sulphate, aluminium and manganese (Table 2.4).

2.2.3 Bethal.

Situated at a sub-station on the outskirts of Bethal, this site was chosen to provide information on the influence of towns on bulk deposition. Low fluoride, potassium and magnesium deposition rates were recorded. The deposition rates of sulphate, nitrate, chloride, calcium and manganese were very constant throughout the study period. Higher deposition rates for chloride and nitrate were noted during summer (Appendix 2: Figures 2.2-2.12).

Winds from the south-westerly to south-easterly sectors were negatively correlated with the deposition of chloride, nitrate, calcium, aluminium, iron and manganese (Table 2.4). No large pollution sources are located in the area to the south of the site (Figure 1.6).

2.2.4 Hendrina.

This site was also placed within a small town. Fluoride was rarely deposited. The deposition rates of chloride,

calcium and manganese did not vary much during the study period. Higher rates of deposition of chloride, nitrate, sulphate, potassium, magnesium and manganese seemed to occur in summer, although nitrate was deposited erratically (Appendix 2: Figures 2.2-2.12). A problem with bird guano was experienced from time to time at this site, providing a possible explanation for the higher potassium deposition.

Wind direction was not significantly correlated to the deposition rates of any species.

2.2.5 Arnot.

The Arnot site was located within the ESCOM township near to the Arnot power station. The deposition recorded is of interest since the site was located very close to a major pollution source.

The deposition rates of all the species were higher than those recorded at the other sites and were very erratic with possible increases during spring and early summer (Appendix 2: Figures 2.2-2.12). A serious guano problem was experienced at this site, possibly accounting for the high and irregular deposition of potassium and sodium.

North-westerly winds were positively correlated with the deposition rates for chloride, sulphate and iron, whereas that for nitrate, potassium, calcium and magnesium were positively correlated to north-easterly winds. Winds from the south-westerly sectors were negatively correlated with the

deposition of chloride, sulphate, potassium, magnesium and manganese (Table 2.4). Very few pollution sources lie to the south of the Arnot site, so lower deposition rates of sulphate and chloride were expected when the wind blew from this direction. The high depositions of calcium, potassium and magnesium during a north-easterly wind were probably related to the location of a large open strip mine to the north of the site.

2.2.6 Kriel.

Located on the outskirts of the ESCOM Kriel township, this site was within a few kilometers of the two large power stations, Kriel and Matla (Figure 1.6).

On average low rates of fluoride and potassium deposition were recorded. Nitrate was deposited in an irregular fashion whereas the deposition rates of sulphate, chloride, calcium and manganese remained reasonably constant throughout the study period. The amount of manganese deposited increased slightly during the summer months (Appendix 2: Figures 2.2-2.12).

Winds from the southern sectors were negatively correlated with the depositions of calcium, whereas easterly winds produced significantly less magnesium (Table 2.4).

2.2.7 Wildebees.

The two large coal liquification plants, Sasol 2 & 3, were situated to the south-west of this site. Placed at an electricity distribution station and within a kilometer or two of

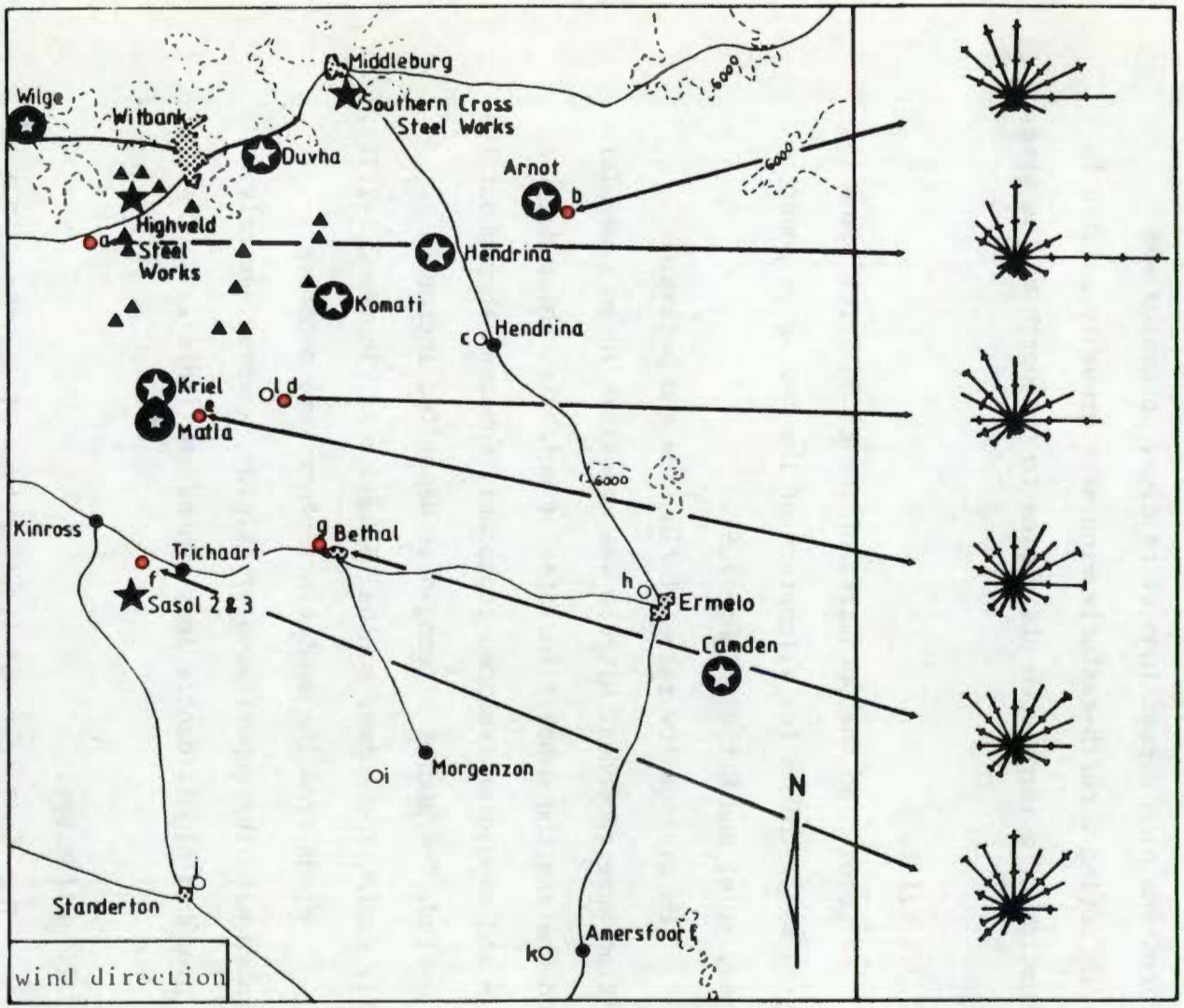


Figure 2.13: Wind roses showing the percentage frequency occurrence of the surface wind directions experienced at the bulk deposition sites during the study period.
The wind roses are marked at 5% intervals.

a railway line and major road, the nitrate deposited at this site was expected to be higher than at the other sites.

No potassium and very little fluoride (except during isolated episodes) were deposited. The deposition rates of chloride, sulphate and calcium were reasonably constant during the study period with a slight increase in sulphate deposition and decrease in chloride deposition during summer. Nitrate depositions were quite constant during the summer and winter months but irregular during spring (Appendix 2: Figures 2.2-2.12).

Winds from the north-west were positively correlated to depositions of nitrate and calcium, presumably due to the locations of the road and railway line. Higher sulphate, iron and aluminium concentrations were expected when the wind blew from the north-eastern sectors implying Komati, Hendrina and Arnot Power Stations as possible sources of these species. Winds from the south-west were negatively correlated with aluminium, iron and manganese depositions (Table 2.4).

2.2.8 Intersite comparisons.

The results of the ANOVA and SNK tests imply that the deposition rates for chloride, sulphate, sodium, potassium, calcium and magnesium were significantly higher at Arnot than at any of the other sites (Appendices 2.1 and 2.2). The deposition of sulphate and chloride at Arnot were correlated with the occurrence of north-westerly winds. Winds from these sectors blew

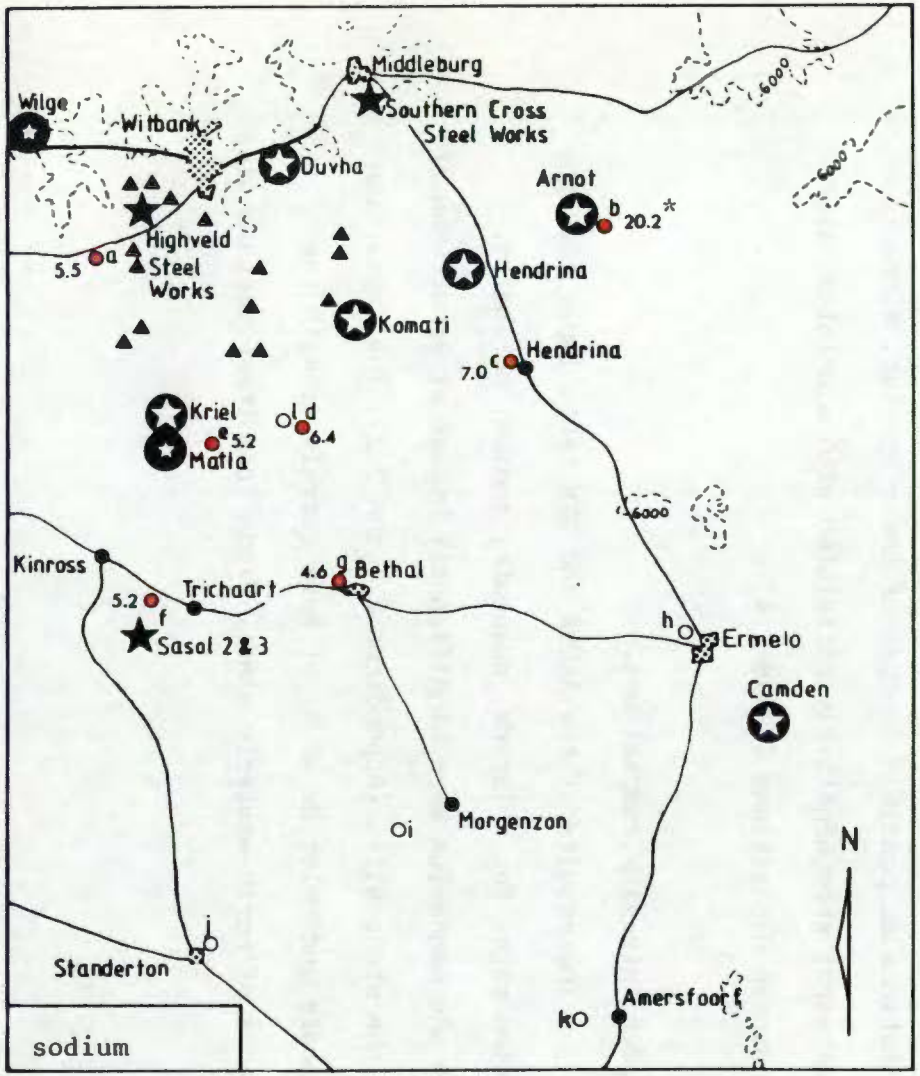


Figure 2.14: The spatial variations in the annual bulk depositions (kg/Ha) of sodium in the eastern Transvaal Highveld.
* The rates recorded at site b may have been biased by the proximity of the site to a large open cast mine.

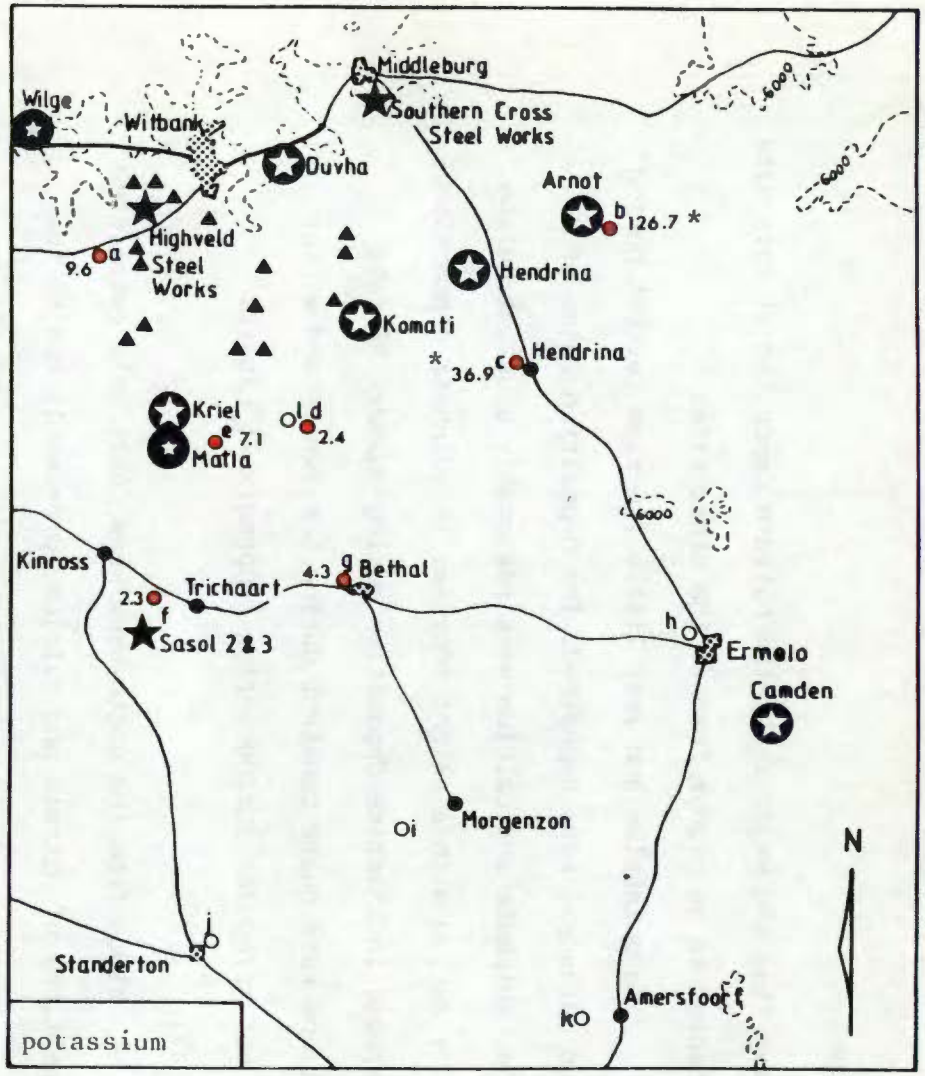


Figure 2.15: The spatial variations in the annual bulk depositions (kg/Ha) of potassium in the eastern Transvaal Highveld.
* These values at sites b and c were most likely biased by guano contamination.

frequently during the study period (Figure 2.13), and it is most likely that the depositions recorded were due to pollution sources to the north-west of the site. The plumes of Arnot Power Station are composed primarily of sulphur dioxide and fly ash and probably provided much of the sulphate measured. The very high depositions recorded were most likely due to the proximity of the stack to the site. Chlorine gases are emitted during the manufacture of iron and steel and it is possible that the chlorides measured at the Arnot originated from the Southern Cross Steel works, a few kilometers to the north-west of the site.

The high sodium, potassium, calcium and magnesium loadings recorded at Arnot were distinctly site specific (Figures 2.14, 2.15, 2.16 and 2.17). Sodium, calcium and magnesium are soil-derived constituents and their origins in the atmosphere are often related to local sources. The correlation of the deposition rates of these and the occurrence of the north-easterly wind, together with the presence of a large open-cast mine to the north of Arnot, implies a localized source of these elements. The high deposition rates of potassium recorded at Arnot together with those for Hendrina were most likely related to the guano problems encountered at these two sites (Figure 2.15). Contamination due to guano has been shown significant for potassium but negligible for other species such as sulphate, chloride or nitrate (Granat, 1982).

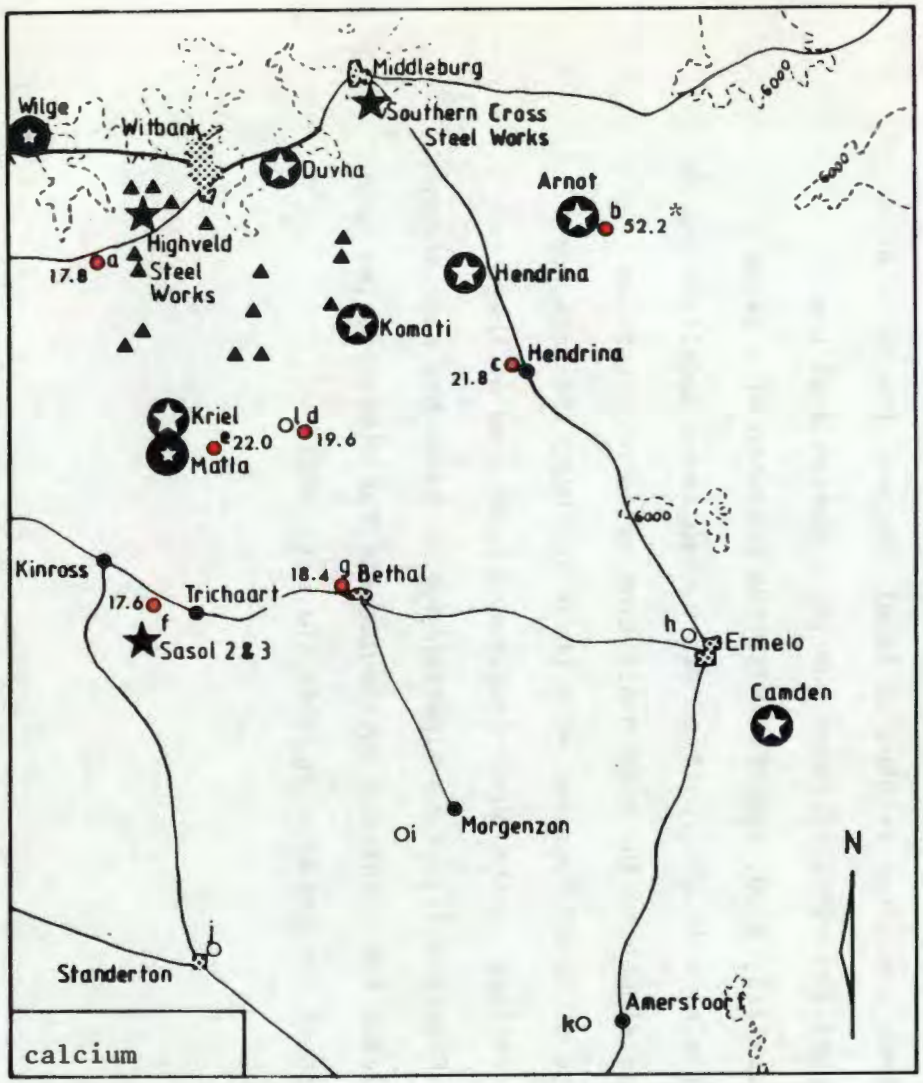


Figure 2.16: The spatial variations in the annual bulk depositions (kg/Ha) of calcium in the eastern Transvaal Highveld.
* The rates recorded at site b may have been biased by the proximity of the site to a large open cast mine.

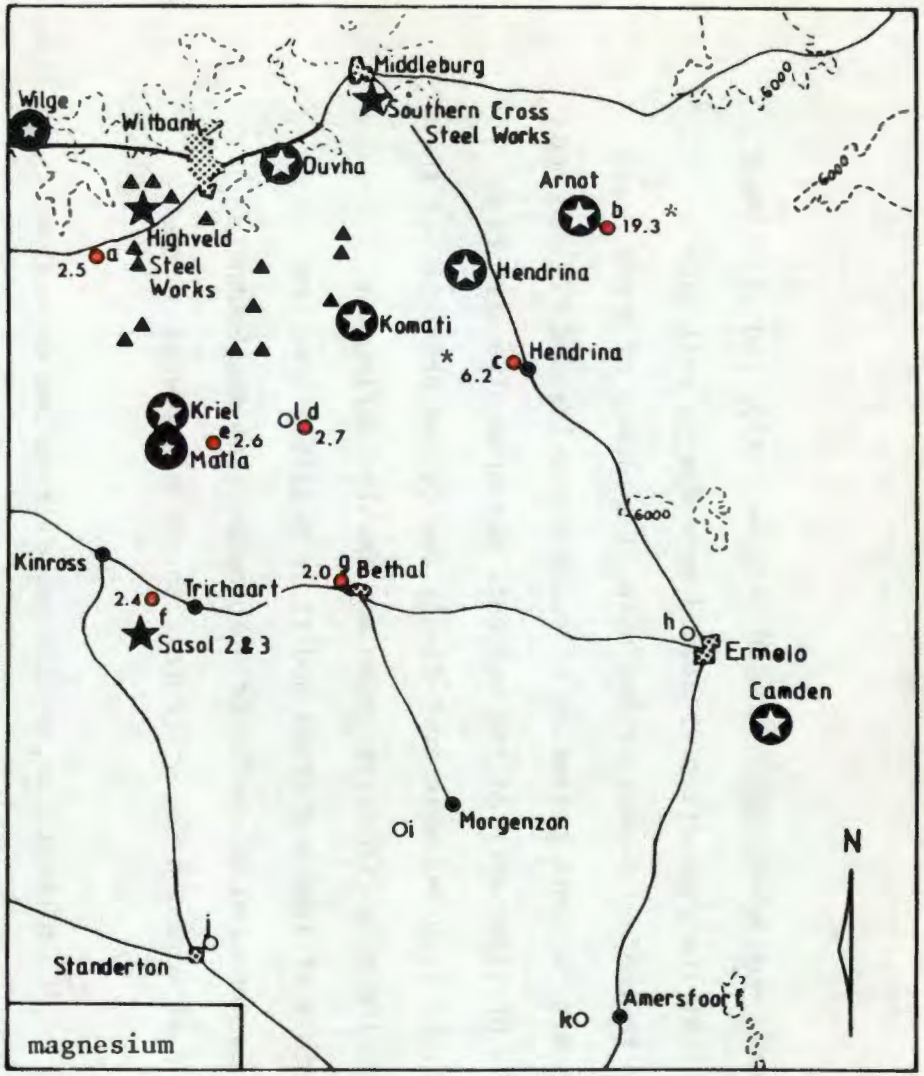


Figure 2.17: The spatial variations in the annual bulk depositions (kg/Ha) of magnesium in the eastern Transvaal Highveld.
* The rates recorded at sites b and c may have been biased by guano contamination.

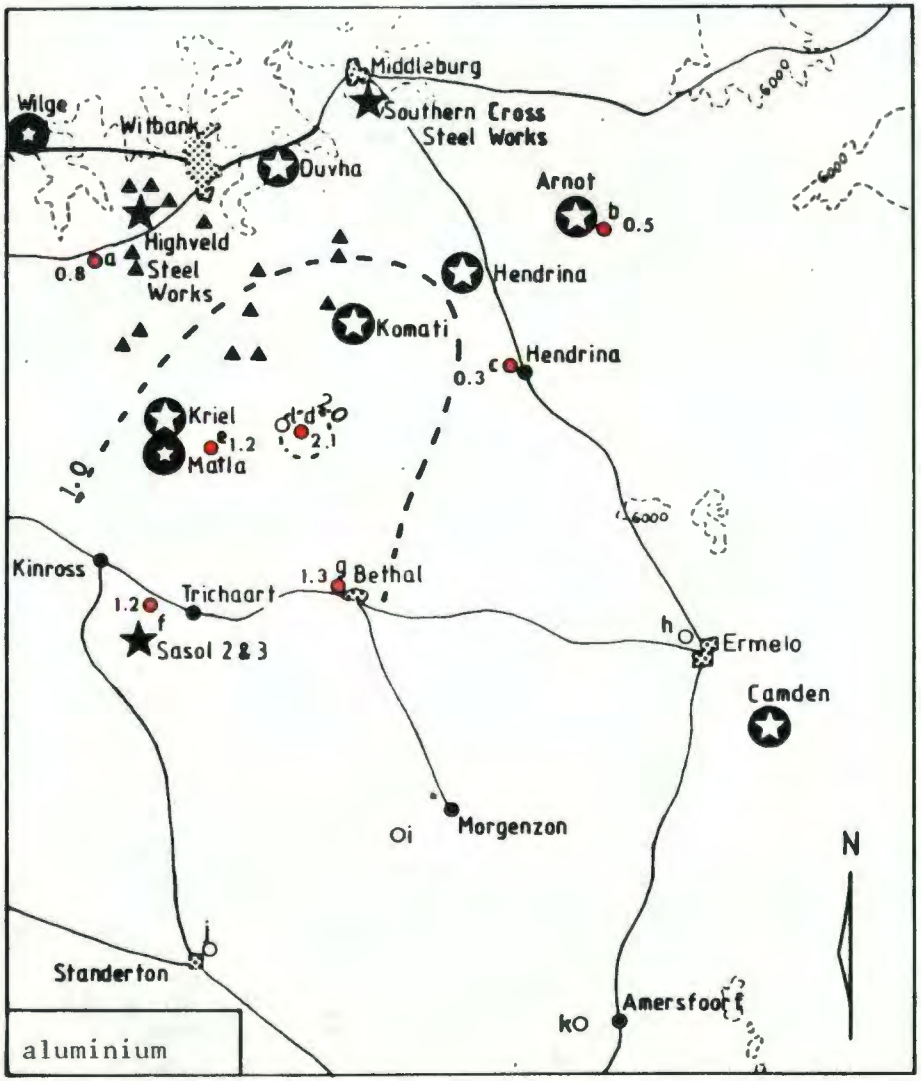


Figure 2.18: The spatial variations in the annual bulk depositions (kg/Ha) of aluminium in the eastern Transvaal Highveld.

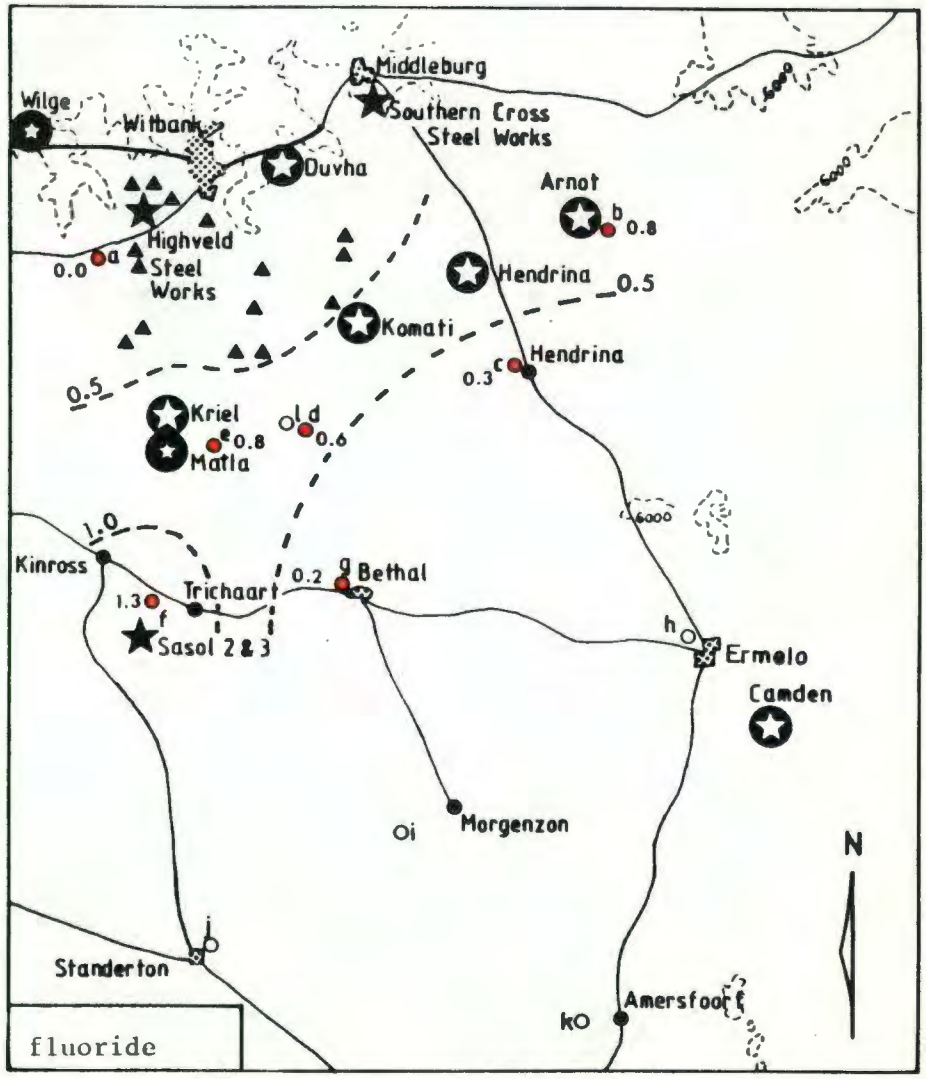


Figure 2.19: The spatial variations in the annual bulk depositions (kg/Ha) of fluoride in the eastern Transvaal Highveld.

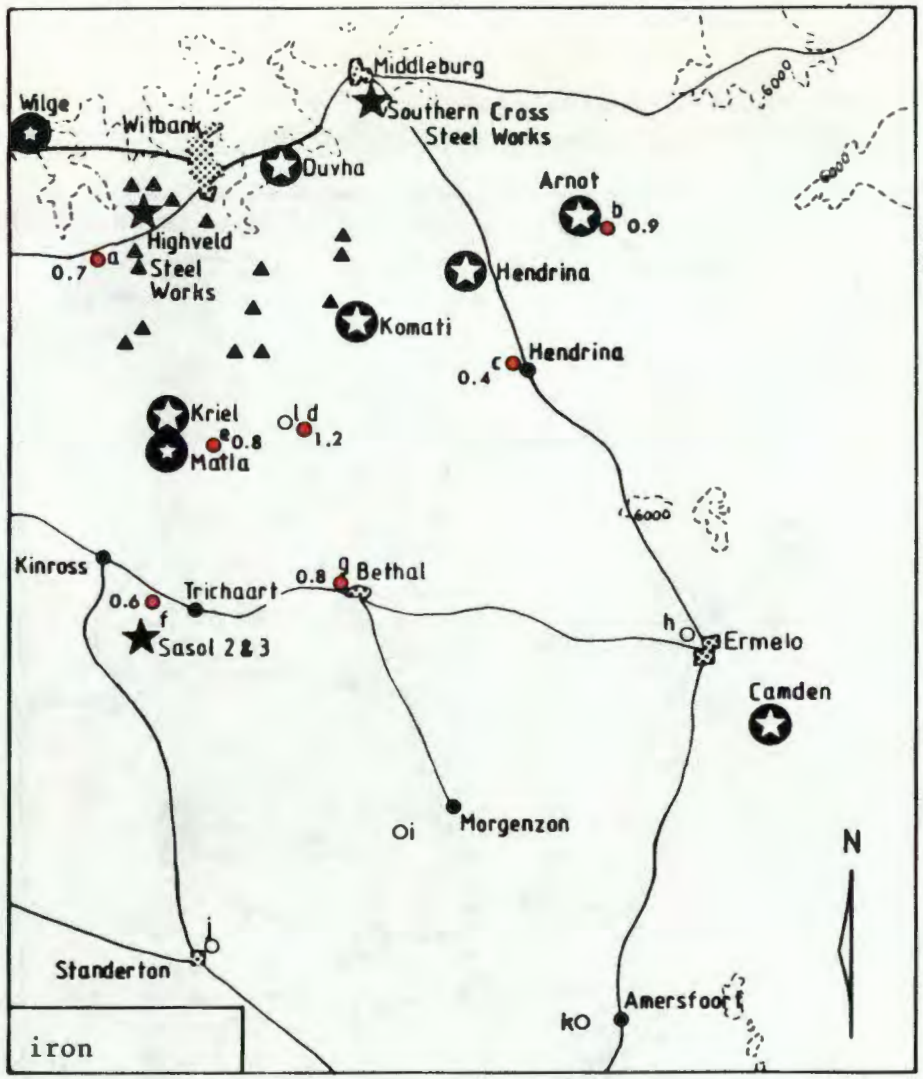


Figure 2.20: The spatial variations in the annual bulk depositions (kg/Ha) of iron in the eastern Transvaal Highveld.

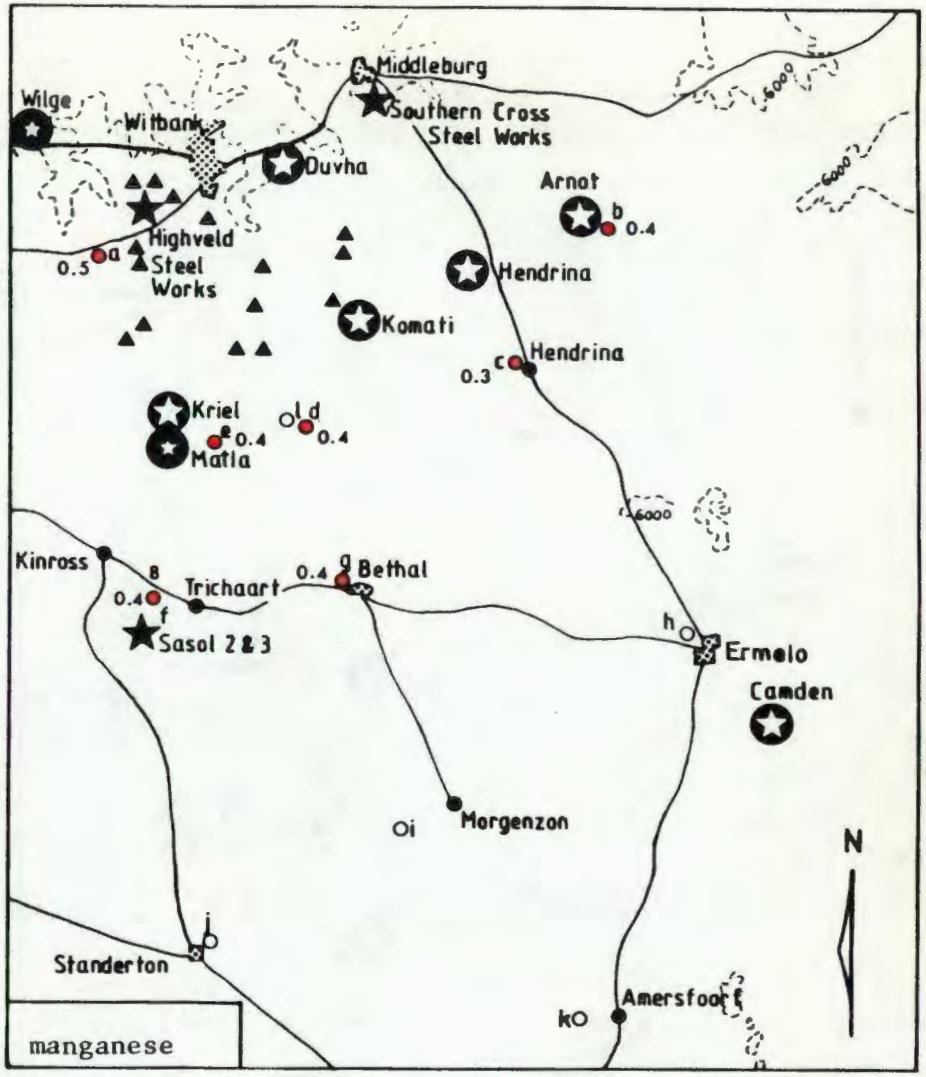


Figure 2.21: The spatial variations in the annual bulk depositions (kg/Ha) of manganese in the eastern Transvaal Highveld.

The deposition rates for aluminium recorded at Elandsfontein were shown significantly higher than those recorded at the other sites (Appendices 2.1 and 2.2). The annual deposition rate at Elandsfontein was distinctly higher than elsewhere (Figure 2.18). Excluding Arnot (which was a special case), the deposition rates for sulphate, fluoride, aluminium and iron at Elandsfontein were also higher than at the other sites. The deposit gauge was located on top of a hillock with major pollution sources to the west, north-west and north-east. The wind blew predominantly from the north-westerly, northerly and easterly directions during the study period (Figure 2.13) and the site was exposed to pollution most of the time. It is also possible that the elevated site intercepted the relatively undiluted plumes.

The sites were chosen to reflect possible differences in deposition between rural (Grootpan and Elandsfontein), urban (Bethal and Hendrina), urban-polluted (Arnot and Kriel) and rural-polluted (Wildebees) areas. The bulk depositions of fluoride, iron and manganese were not influenced by these local sources. The homogeneity of the depositions are well illustrated by the spatial distributions of the annual bulk deposition rates (Figures 2.19, 2.20 and 2.21). With the exception of that recorded at Arnot, the bulk depositions of sodium, potassium, calcium and magnesium were also uniform over the study area (Figures 2.14-2.17). The depositions of chloride and sulphate were on average significantly higher close to a power station

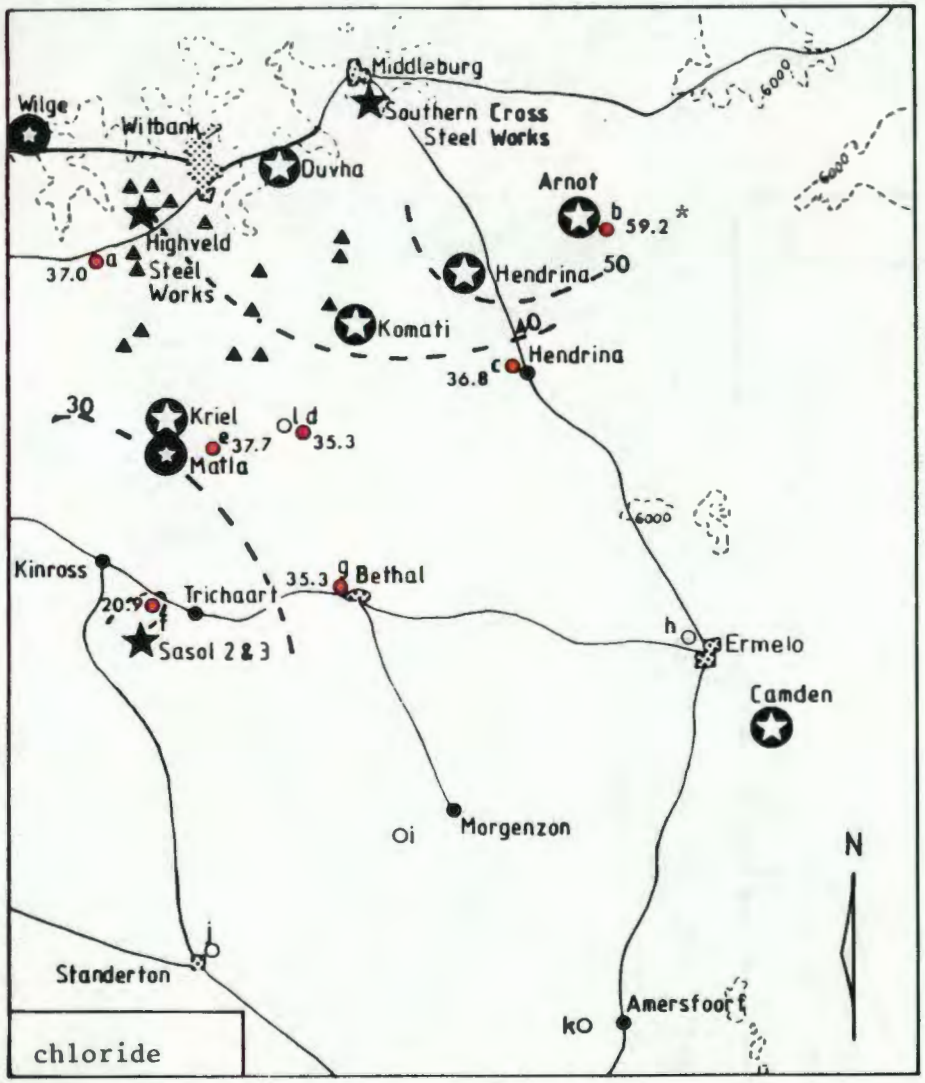


Figure 2.22: The spatial variations in the annual bulk depositions (kg/Ha) of chloride in the eastern Transvaal Highveld.

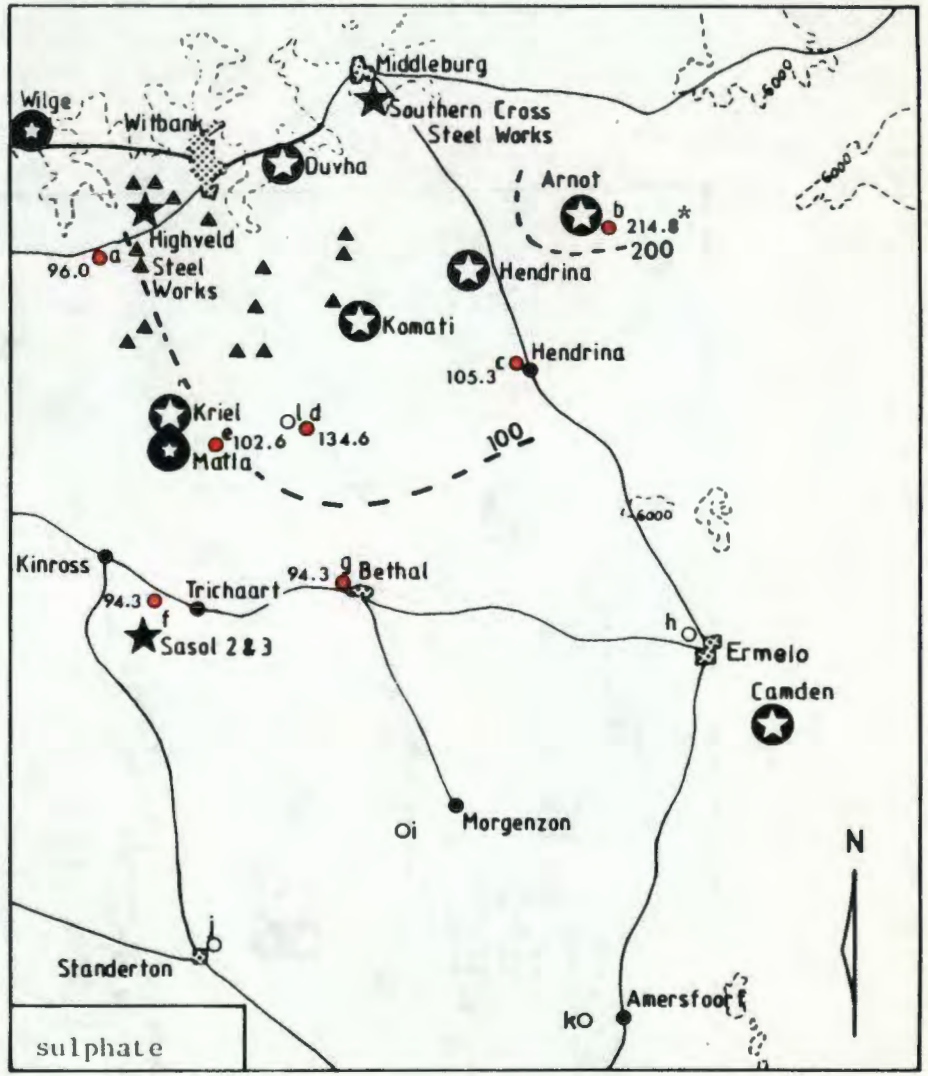


Figure 2.23: The spatial variations in the annual bulk depositions (kg/Ha) of sulphate in the eastern Transvaal Highveld.

* The rates recorded at site b are most likely related to the proximity of Arnot Power Station.

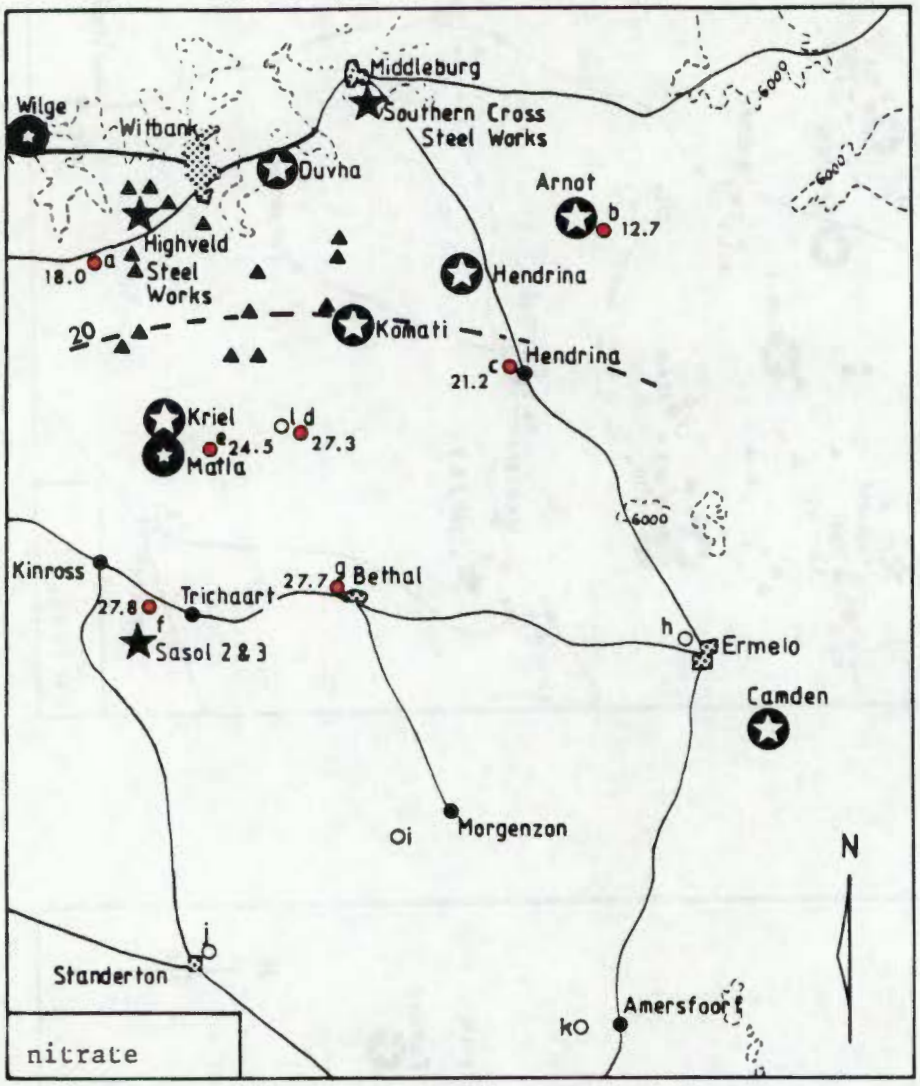


Figure 2.24: The spatial variations in the annual bulk depositions (kg/Ha) of nitrate in the eastern Transvaal Highveld.

stack (Arnot), and if the spatial distributions of the annual bulk depositions are considered, there is a decrease in deposition with distance from the pollution sources (Figures 2.22 and 2.23). The deposition of nitrate seems to be related to the proximity and magnitude of vehicular traffic and therefore the local influence of towns and roads can not be ignored (Figure 2.24).

2.2.9 Temporal Comparisons.

The deposition rates of fluoride, nitrate, aluminium, iron and manganese varied significantly from one exposure period to the next (Appendix 3.1). When related to season of the year and dominant wind directions, it was noticed that the deposition of fluoride (Appendix 3.3) was higher in summer (easterly to north-easterly winds) than in winter (south-westerly to north-westerly winds).

The deposition of nitrate showed less definite trends although a difference between summer and winter and south-westerly winds and winds from the northern sectors could be identified (Appendix 3.4). Since certain sites were located close to roads and areas of intense vehicular activity, these results may be inconsequential.

The deposition of aluminium showed no definite trends with respect to season and wind direction (Appendix 3.5). Iron deposition increased during the summer months with higher values

when the wind blew from the northern to eastern sectors (Appendix 3.6). Manganese showed no depositional trends except a slight increase during the summer (Appendix 3.7).

2.3 DISCUSSION.

The spatial distributions of the bulk depositions of fluoride, iron and manganese and, if the data from Arnot is ignored, sodium, potassium, calcium and magnesium were uniform. There is no evidence of spatial gradients in the bulk depositions of these elements. The even distribution of the soil-derived constituents may be explained by the homogeneous nature of the geology of the area (shale, sandstone, gritstone and coal, 1:1 000 000 Geological Map of Southern South Africa, 1970), but since the power of wind erosion may vary substantially on a spatial scale, other sources (such as fly ash) may be important. The origins of fluoride, iron and manganese were most likely anthropogenic. The even topography of the study area together with the similar deposition rates recorded at the sites excluding Arnot imply that the sites had the same potential for deposition and the study area was covered by a chemically homogeneous smog.

The eastern Transvaal Highveld experiences a deep and stable surface inversion during the winter that can reach 300 m high (Venter et al, 1977). Most plumes will be trapped below the inversion cap with little dilution and horizontal transport. In

summer, extensive vertical mixing during the day creates a well mixed lower atmosphere often capped by a subsidence inversion in the upper layers.

These conditions could be instrumental in creating a well mixed pollution layer in the near vicinity of major industrial centres. It is possible that the long range transport of plumes is severely limited during both summer and winter. The presence of a homogeneous smog encompassing at least the study area is therefore possible.

The annual deposition rates of sulphate and chloride decreased to the south and south-west, and those for nitrate increased to the south of the Witbank-Middleburg Industrial complex. Although these trends were statistically insignificant, the differences in annual bulk deposition between the sites reached 30 kg/Ha/yr for sulphate, 17 kg/Ha/yr for chloride and 10 kg/Ha/yr for nitrate. The spatial trends exibited by the deposition of nitrate may be inconsequential since the sites to the south and south-west of the study area were exposed to much more vehicular traffic than those towards the north. The decrease in the deposition of sulphate and chloride with distance from the pollution complex may be related to the homogeneity of the pollution layer over the study area, conversion pathways, deposition mechanics and the efficiency of the sampling technique used.

Deposit gauges sample the deposition of large particles and rain-water effectively. Small particulates such as sulphate

and chloride are often not realistically sampled. The adsorption of sulphur dioxide onto large fly-ash particles and the subsequent catalyzed oxidation is considered by some as an important removal mechanism close to the pollution source (Ananth, et al, 1977; Newman, 1981; Record, 1981; Dlugi et al, 1983; Oppenheimer, 1983). This process may be particularly important in the Transvaal Highveld since the air is often very dry (Mamane et al, 1979). These sulphate depositions would be efficiently sampled by deposit gauges.

The deposition of sulphate and chloride may also have originated from gaseous absorption by the trapping agent during exposure. The aqueous absorption and subsequent oxidation of sulphur dioxide has been well documented and is considered a possible source of sulphate in samples with an extended exposure period (Peden et al, 1978; Glover et al, 1979; Penkett et al, 1979b; Fisher, 1982; Reda et al, 1982; Altwicker, 1983; Barrie et al, 1983).

Therefore, the bulk deposition sites located close to pollution sources, would record high sulphate values since the large particles settle close to the stack and any atmospheric instability would bring the relatively undiluted plume into contact with the deposit gauge thereby enhancing the gaseous absorption of sulphur dioxide. The ambient concentrations of sulphur dioxide (and other gases in the plumes) decrease with distance from the source particularly in a well mixed atmosphere. The deposit gauges located further from the source area would

Table 2.5 : The annual bulk depositions (kg/Ha/yr) of the ions measured at the seven sites in the eastern Transvaal Highveld during the year August 1982 to August 1983.

Element	Annual Deposition (kg/Ha/yr)						
	Grootpan	Elandsftn	Bethal	Hendrina	Arnot	Kriel	Wildebees
Fluoride	0.0	0.6	0.2	0.3	0.8	0.8	1.3
Chloride	37.0	35.3	35.3	36.8	59.2	37.7	20.9
Nitrate	18.0	27.3	27.7	21.2	12.7	24.5	27.8
Sulphate	96.0	134.6	94.3	105.3	214.8	102.6	94.3
Sodium	5.5	6.4	4.6	7.0	20.2	5.2	5.2
Potassium	9.6	2.4	4.3	36.9	126.7	7.1	2.3
Calcium	17.8	19.6	18.4	21.8	52.2	22.0	17.6
Magnesium	2.5	2.7	2.0	6.2	19.3	2.6	2.4
Aluminium	0.8	2.1	1.3	0.3	0.5	1.2	1.2
Iron	0.7	1.2	0.8	0.4	0.9	0.8	0.6
Manganese	0.5	0.4	0.4	0.3	0.4	0.4	0.4

sample less particulate matter (due to the inefficiency of deposit gauges in sampling small particles) and less gaseous absorption is anticipated. The spatial trends exibited by the deposition of sulphate and chloride in the eastern Transvaal Highveld are therefore more than likely caused by the measuring technique used.

The roles of wet and dry deposition can be briefly considered since the study area receives summer rainfall only. From the temporal trends, it is obvious that for sulphate and chloride the deposition rates do not vary much according to season. This implies that either all the sulphur and chloride in the atmosphere is being deposited or that the decrease in potential dry deposition in summer (due to increased atmospheric instability and plume dilution) is compensated for by the wet deposition component. Fluoride, iron and manganese showed significant temporal variations that could be related to season and dominant wind direction. These elements were deposited in greater amounts during the summer months, possibly implying a significant contribution by wet deposition. Although nitrate showed temporal variations these were most likely biased due to the presence of extensive vehicular activity near some sites.

The annual depositions (kg/Ha/yr) measured at the seven sites are compared with the results of a few bulk deposition networks in other parts of the world (Tables 2.5 and 2.6). The

Table 2.6 : The annual bulk depositions (kg/Ha/yr) recorded in other areas of the world.

Site	Description	Bulk depositions (kg/Ha/yr)						
		$[Cl^-]$	$[NO_3^-]$	$[SO_4^=]$	$[Na^+]$	$[K^+]$	$[Ca^{++}]$	$[Mg^{++}]$
North America[1]	Heavy Industrial			1-?				
Europe[1]	Heavy Industrial			20-200				
North America[1]	Rural			1-50				
Europe[1]	Rural			2-70				
North Altantic[1]	Rural			1-10				
Other Oceans[1]	Remote			0.1-3.0				
Continents[1]	Remote			0.1-9.0				
Netherlands[2]	Industrial		~20	~250				
ELA Ontario[3]		2.82	9.23	43.72	1.53	1.04	3.62	0.93
New York State[4]		10.65	29.13	49.78	1.74	1.17	10.52	1.75
Hubbard Brook, USA[5]		6.23	19.44	38.29	1.58	0.93	2.12	0.53
Coweeta SC, USA[6]		15.63	11.37		3.62	1.75	4.91	1.09
Walker Branch, USA[6]			16.99		3.83	3.05	15.79	2.94
Southern Norway[7]		0.83 175.25	3.19 58.08	7.87 98.34		0.36 6.86	0.47 8.21	0.23 14.22
Iowa, USA[8]	Agriculture		21.29	37.23				

[1]Record (1981) [2]van Aalst (1983) [3]Schindler et al (1976) [4]Likens (1972)
[5]Likens et al (1977) [6]Swank et al (1976) [7]Wright et al (1978) [8]Tabatabai et al (1976)

annual deposition of chloride in the eastern Transvaal Highveld was comparable to that measured by Wright et al (1978) in Norway. The nitrate depositions recorded at Grootpan and Hendrina were similar to those of the Netherlands whereas the depositions measured at the remaining sites compared with those for Upstate New York. The annual deposition of sulphate measured at Arnot was similar to the maximum annual deposition recorded in the industrialized centres of Europe. The sulphate measured at the other sites compared with that of southern Norway and were on average twice that recorded at any of the other rural areas.

The deposition of the cations were on the whole comparable with other places in the world although Arnot received substantially greater deposition in some cases.

2.4 SUMMARY.

The results imply that the maximum deposition to a water surface occurred close to the stack. On a regional scale, the influence of towns seemed negligible with the exception of nitrate deposition. On average, slightly higher depositions of fluoride, iron and manganese occurred in summer whereas sulphate and chloride deposition rates were constant throughout the year. Dry deposition seems to be the more important removal process as anticipated by Venter et al (1977). Surface winds from the southern, south-western and south-eastern sectors were related to lower deposition rates at most sites whereas northerly, north-westerly and north-easterly winds correlated to higher depositions. Except for the influence of Camden power station in the south-east, most anthropogenically produced species seemed to originate from the direction of the Witbank-Middleburg Power and Industrial Centre.

The study area may have been covered by a chemically homogeneous layer of smog. The deposition of fluoride, iron, manganese, sodium, potassium, calcium and magnesium did not vary much spatially. The spatial trends in sulphate and chloride depositions may be related to the limitations of the sampling technique.

The annual depositions recorded during the study period were comparable to those of industrialized centres of Europe and North America as well as southern Norway. The sulphate values may be high due to hygroscopic growth over smooth water surfaces, but it is disturbing that a basically rural area can be classified as industrialized from a depositions point of view.

CHAPTER 3.

WET DEPOSITION
in the
EASTERN TRANSVAAL HIGHVELD.

The quality of the rain-water falling in the eastern Transvaal Highveld was studied from February to May, 1984. The nature and severity of these depositions were considered.

3.1 METHODOLOGY.

The rain storms were individually sampled using Aero-chem Metrics Wet/Dry Precipitation Collectors. The time the event started, its duration, intensity and volume were recorded by OSK tipping bucket rain gauges. The free acidity of the rain-water (as pH) was determined in the field soon after the end of the event. The samples were stored for chemical analysis, but due to constraints on laboratory facilities, dry depositions were not monitored.

The choice of a study area was complicated by several factors. Firstly, the literature links acid precipitation to the long range transport of pollutants. The bulk deposition study area was therefore, unsuitable for monitoring the wet deposition of pollutants from the Witbank-Middleburg Power and Industrial Complex.

Secondly, the eastern Transvaal Highveld experiences rapid mixing of the lower atmosphere during summer and it is not unusual for the plumes to be looping to the ground before 09h00. Therefore the pollutants emitted in this region during the day may have a relatively short residence time in the atmosphere. At night, with the development of a weak surface inversion, the pollutants may be trapped aloft for longer periods.

Thirdly, the rain falling in this area occurs in the form of short, intense thunderstorms that usually develop towards the late afternoon. Those areas closer to the escarpment (such as Ermelo or Amersfoort) do experience long periods of soft, soaking rain. Both rain types enhance the absorption and oxidation of sulphur dioxide.

Considering that the lower atmosphere is well mixed during the day and that the formation of clouds occurs at the peak of this turbulent activity, wet deposition may remove most of the pollutants emitted from the Witbank-Middleburg Region in the near vicinity of the sources.

These considerations, together with the interest shown in the pollution levels of the area and the prevalent north-westerly winds in the upper levels, prompted the choice of Bethal, Ermelo, Amersfoort, Standerton and Morgenzon as the general study area (Figure 1.6). Situated one to two hundred kilometers south-east of Duvha Power Station (often regarded as the centre of the eastern Transvaal Highveld power and industrial complexes), there are no large scale pollution sources within the area besides those related

Table 3.1 : The physical characteristics of the five wet deposition sites.

Characteristics	Amersfoort	Bethal	Ermelo	Morgenzon	Standerton
Wind Data	N	N	N	N	N
Access Road	grassed foot path	dust road	dust road	grassed foot path	dust road
Local Influences:					
Industry	N	N	N	N	N
Towns/Cities	N	N	N	N	Y
Road/Rail	tarred road 1 km, dust road 1 km	tarred road 5km, dust road 1km	N	tarred road 2km	dust road 1km
Landuse	fallow veld	farm yard	farm yard	fallow veld	small holding fallow field
Ground cover	short veld grass	short grass	short grass	short veld grass	fallow lucerne field
Overhead Obstacles	N	N	power line	N	telephone and power lines

to small urban clusters. The terrain is relatively undulating and the land is cultivated with corn and sun-flowers and livestock farming is practised.

The locations of the sites were determined by the proximity of local pollution sources and the availability of responsible site personnel to service the equipment and accurately measure field pH. A list of those farmers, who had been involved with collecting information for a scientific organization in the past was obtained. The general location of each farm to electrical and telephone networks, roads, urban activities and any local pollution sources was determined and using a helicopter, the sites were surveyed for regional representation. Fortunately the owners of those farms which satisfied the most siting criteria, proved to be interested and capable site operators. The site characteristics are presented in Table 3.1, and aerial photographs of the Amersfoort, Morgenzon and Standerton sites in Figures 3.1-3.3.

3.1.1 Experimental Procedures.

The Aero-chem Metrics Precipitation Collector, tipping bucket and standard garden rain gauges were placed in an easily accessible field within 200 m of a 220V power outlet (Figure 3.4).

The site personnel were encouraged to collect the sample as soon after the end of the event as possible. The volume of rain that fell was read from the standard garden rain gauge and

Figure 3.1: An aerial photograph of the Amersfoort site, showing the flatness of the terrain and the general representativeness of the site for the area as a whole. The arrow indicates the location of the site.

Figure 3.2: An aerial photograph of the Morgenzon site, showing the flatness of the terrain and the general representativeness of the site for the area as a whole. The arrow indicates the location of the site.

Figure 3.3: An aerial photograph of the Standerton site, showing the flatness of the terrain and the general representativeness of the site for the area as a whole. The arrow indicates the location of the site.

Figure 3.5: The layout of the field laboratory showing the Radiometer-Copenhagen PHM83 pH meter.

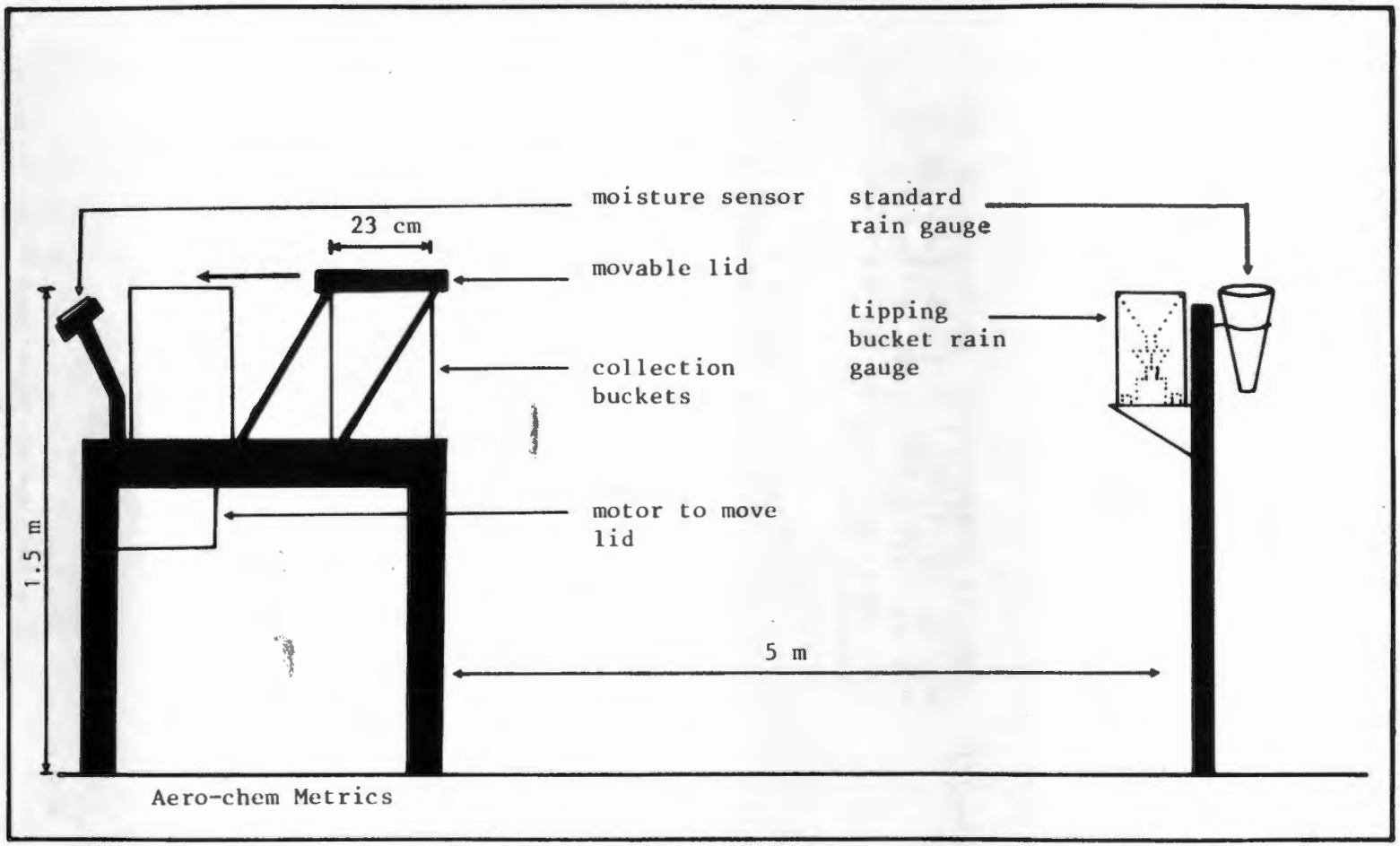


Figure 3.4: A field site showing the Aero-chem Metrics wet/dry precipitation collector and the tipping bucket and standard rain gauges.

recorded. The gauge was then emptied. The tipping bucket rain gauge was serviced once a week, during which the clock was wound and the chart replaced.

The field laboratory was set up in a clean, but little-used room such as that in which the milking apparatus were stored (Figure 3.5). The pH of the sample was measured immediately after the servicing of the site. The remaining sample was decanted into two polyethylene bottles, one was sealed and stored in the refrigerator and the other was preserved with chloroform and stored on the shelf. If too little volume was collected, the determination of pH had first preference followed by the refrigeration of any remaining sample.

The sites were visited once a week to deliver clean buckets and sample bottles and to collect the stored samples, any description forms, the tipping bucket rain gauge charts and the used buckets. The samples were delivered to the laboratory immediately where they were kept in the refrigerator until analysed (Table 2.4).

Surface wind direction was not available at the sites. The local Weather Bureau stations were either poorly sited, did not measure ground level wind or were too far away from the acid rain site for reliable data extrapolation. Upper air wind data (1000 m above ground level) for the 01h00 and 14h00 soundings at Irene (south of Pretoria) were obtained from the Meteorological Office at Jan Smuts Airport, Johannesburg.

It was intended to commence sampling in October 1983, but shipping delays resulted in the Aero-chem Metrics Precipitation

Collectors only arriving in January, 1984. The sites were all operational by the end of the first week in February, 1984 and sampling continued until the last storm of the season in May, 1984.

3.1.2 Data Presentation.

The sulphate values discussed are in terms of total sulphur, owing to the tendency for dissolved sulphur dioxide to oxidize in the samples awaiting analysis. The volume weighted average concentrations of the ions (μeq/l) are presented spatially. The temporal trends in concentration (μeq/l) during an extended wet period are presented in the form of bar graphs.

The spatial variations in both the concentrations and loadings ($\mu eq/m^2$) of the wet depositions were considered using 1X1 ANOVAs without repetitions. Spatial and temporal variations between specific events were studied using 2X2 ANOVAs without repetitions. Since rain is sporadic and localized in nature, the same event rarely occurred at all the sites similtaneously and these ANOVA tables were constructed from rain periods during which at least three sites sampled an event. The missing data were approximated using an average rain volume for the period together with the volume weighted average for the site. The usual methods proposed by Snedecor (1956) and Steel et al (1960) were not used because these utilized marginal totals, which were very different for each site, and unrealistic estimations were generated.

The relative contributions by the acidic anions (fluoride, acetate, formate, chloride, nitrate and sulphate) to the

free acidity of the samples, were considered using the ratios ($[X]/[H^+]$) of the concentration of the anion (μeq/l) to that of the hydrogen ions (μeq/l as calculated from pH). If the individual ratios were less than 1, there was not enough of any one anion to support all the free acidity. If the sum of all the ratios were less than 1, insufficient strong and weak acids were present to support all the free acidity. If the ratios or sums of ratios were greater than 1, enough of the anions were present to account for the free acidity (Galloway et al, 1982). These ratios were calculated for each event and for the volume weighted averages.

The role of storm characteristics such as duration, intensity and volume were considered using correlation matrices and regression analyses. The association of free acidity (as $[H^+]$) to storm characteristics and other anions and cations was determined using stepwise multi-linear regression analyses. The statistical analyses were performed using the HP9816 statistical package and Sokal et al (1969).

3.2 DATA QUALITY.

Those samples analysed within one hour after the end of the event or with a pH of less than 4.50 pH units were considered chemically representative of the rain event (Galloway et al, 1976; Böhm, 1984). 84.2% of the pH measurements recorded at Amersfoort, 80.0% at Ermelo, 63.6% at Morgenzon and 66.7% at Standerton fell

Table 3.2 : The magnitude and statistical significance of the systematic errors between the techniques used in determining the rain volume, sample pH and hydrogen ion concentrations (Mann Whitney U Tests; ***, no difference between the data sets at $p<0.01$; **, no difference between the data sets at $p<0.05$). The techniques compared for determining the rain volume are standard rain gauges read manually by the site personnel (fvol) versus automatically recording tipping bucket rain gauges (lvol). Field pH measurements under uncontrolled conditions (fpH) are compared with pH measurements performed in the laboratory (lpH) and the hydrogen ion concentrations of the samples as calculated from field ($f[H^+]$) and laboratory ($l[H^+]$) pH are compared.

Site	X fvol-X lvol	X fpH-X lpH	X $f[H^+]$-X $l[H^+]$
Amersfoort	- 0.9 (***)	0.10 (***)	- 0.32 (***)
Ermelo	0.0 (***)	0.29 (***)	- 27.30 (***)
Morgenzon	- 3.1 (**)	0.04 (***)	- 15.72 (***)
Standerton	- 0.6 (***)	- 0.41 (**)	1.77 (***)

within this category. All of the samples collected at Bethal had pH values less than 4.50 units.

There were no significant differences between field and laboratory pH measurements at Amersfoort ($p<0.01$), Ermelo ($p<0.01$), Morgenzon ($p<0.05$) and Standerton ($p<0.01$) (Table 3.2). A similar result was obtained for hydrogen ion concentrations (Table 3.2). On average the field measurements underestimated the free acidity by 0.1-0.3 pH units. These results correspond to those by McQuaker et al (1983).

The differences between the volume of rain recorded by the site operator using the standard garden rain gauge and that of the tipping bucket rain gauge were also considered (Table 3.2). No significant differences between the two data sets could be established ($p<0.01$).

The quality of the chemical data was controlled by the analytical chemists of the Department of Chemical Test and Research at ESCOM, Rosherville to within instrument error (Table 2.3).

Table 3.3 : The percentage of rain events that occurred during the night, the day or both, together with their dominant upper air wind directions, and the range, arithmetic mean and standard error of the storm duration, volume and intensity, with the average upper air wind direction for the study period. The upper air wind directions were extrapolated from Jan Smuts Airport, Johannesburg.

Site	Occurrence	Dominant Wind Dir 1000 m agl		Duration (hours)	Volume (mm)	Intensity (mm/hr)	Av Wind Direction 1000 m agl
Amersfoort	night 50%	SW, NW	max	32.25	20.2	18.60	
	day 31%	WNW-NNW	min	0.50	0.8	0.20	
	both 19%	NE	[1]mean	8.71	7.6	2.98	NNW-NW
			[2]SE x	2.13	1.4	1.18	
Ermelo	night 47%	N-NE,S-SE	max	26.25	39.0	17.80	
	day 37%	NNW	min	0.25	1.6	0.34	
	both 16%	NW	mean	7.35	8.8	2.97	NNW-NE
			SE x	1.72	2.5	1.00	
Morgenzon	night 25%	NNE	max	39.25	12.8	22.15	
	day 63%	WNW-NNW	min	0.50	1.5	0.71	
	both 12%	NNE-NNW	mean	9.87	9.2	4.16	NNW
			SE x	4.68	2.7	2.58	
Standerton	night 56%	NW	max	34.50	29.8	11.50	
	day 22%	NW-SW	min	0.50	3.4	0.60	
	both 22%	NNE-NNW	mean	9.67	10.4	3.94	NW-NNE
			SE x	4.49	2.9	1.19	
Bethal	night -		max	-	50.0	-	
	day -		min	-	5.0	-	
	both -		mean	-	15.4	-	-
			SE x	-	11.6	-	

[1]arithmetic mean [2]standard error of the mean

3.3 RESULTS.

3.3.1 Amersfoort.

The site was located on the farm Bergvliet 10-15 km south of the town Amersfoort. The nineteen events sampled varied from intense thunderstorms of a few minutes to several days of soft, continuous rain. The average duration of an event was 8.3 hours with an average volume of 7.64 mm and an average intensity of 2.98 mm/hr. Most of the events occurred at night. The upper air wind (1000 m agl) blew mainly from the north-western sector during rain days and nights (Table 3.3).

The precipitation was acidic with the pH ranging from 3.73 to 5.51 units. The volume weighted mean for the study period was 4.34 pH units. The major ionic constituents were sulphate (0-369.96 μeq/l; vol wt av=92.92 μeq/l), hydrogen ions (3.09-190.55 μeq/l; vol wt av=45.71 μeq/l), nitrate (0-169.99 μeq/l; vol wt av=37.27 μeq/l) and ammonium ions (0-71.08 μeq/l; vol wt av=17.98 μeq/l) (Table 3.4). Very low concentrations of fluoride, acetate, aluminium, calcium, potassium, iron and manganese were present in the samples collected and few events deposited potassium and calcium.

The concentrations of chloride ($n=20$, $p<0.01$) and sodium ($n=20$, $p<0.05$) were inversely proportional to the volume of rain that fell implying a dilution effect possibly due to complete removal of these species from the air mass during the

Table 3.4 : The range, arithmetic mean and standard error and the volume weighted averages for the various chemical species (μeq/l) detected in the rain water sampled in the eastern Transvaal Highveld from February to May, 1984.

Site		pH	Concentrations in μeq/l														
			$[H^+]$	$[F^-]$	[Ac]	[For]	$[Cl^-]$	$[NO_3^-]$	$[SO_4^=]$	$[Na^+]$	$[NH_4^+]$	$[K^+]$	$[Ca^{++}]$	$[Mg^{++}]$	$[Al^{+++}]$	$[Fe^{+++}]$	$[Mn^{++}]$
Amersfoort	max	3.72	190.55	12.10	22.03	29.99	29.05	169.99	369.97	30.88	71.08	4.09	12.97	140.67	54.48	6.98	11.28
19 events	min	5.51	3.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	mean	4.40	39.81	1.45	2.82	10.43	8.50	49.02	117.22	5.02	25.49	0.46	1.75	9.21	5.05	0.64	0.99
	SE x	0.10		0.62	1.53	3.36	2.00	10.57	21.83	1.63	5.05	0.26	0.66	7.11	2.68	0.35	0.56
	VW x	4.34	45.71	0.60	1.34	6.74	4.15	37.27	92.92	2.03	17.98	0.13	0.97	8.44	2.39	0.24	0.40
Ermelo	max	3.80	158.49	8.42	14.06	50.65	38.64	284.65	551.52	25.66	140.50	6.90	6.49	36.20	32.35	2.42	1.89
19 events	min	6.56	0.27	0.00	0.00	0.00	2.26	1.77	3.33	0.00	6.11	0.00	0.00	0.00	0.00	0.00	0.00
	mean	4.46	34.67	2.09	4.08	16.53	11.37	73.12	148.22	5.63	39.72	1.51	0.75	4.21	5.59	0.65	0.37
	SE x	0.16		0.64	1.07	4.83	2.50	20.14	30.79	1.62	8.82	0.50	0.41	2.13	1.73	0.18	0.10
	VW x	4.23	58.88	1.54	3.00	15.91	7.93	71.68	128.03	3.35	30.82	1.14	0.50	5.88	3.42	0.37	0.40
Morgenzon	max	3.93	117.49	20.53	5.08	467.90	23.41	279.49	434.10	10.44	118.84	3.58	19.46	17.27	30.80	2.15	2.33
11 events	min	4.84	14.45	0.00	0.00	0.00	1.97	8.39	30.40	0.00	6.11	0.00	0.00	0.00	0.00	0.00	0.01
	mean	4.27	53.70	3.47	1.38	77.76	11.70	91.78	181.59	4.48	54.81	1.40	3.57	1.92	10.73	0.72	0.53
	SE x	0.09		1.98	0.89	65.91	2.31	27.51	38.99	1.20	13.13	0.45	1.95	1.71	3.70	0.25	0.23
	VW x	4.39	40.74	1.17	0.78	61.36	7.07	43.85	104.01	2.11	29.57	0.60	2.00	0.56	3.85	0.29	0.14
Standerton	max	4.00	100.00	3.16	3.90	84.87	11.56	151.76	255.25	5.22	81.64	2.30	3.49	41.13	19.90	1.88	0.62
9 events	min	4.85	14.12	0.00	0.00	0.00	2.82	10.16	34.56	0.00	13.88	0.00	0.00	0.00	0.00	0.00	0.11
	mean	4.45	35.48	1.11	1.07	21.53	6.77	66.27	137.87	3.14	43.44	0.48	1.61	8.97	5.32	0.52	0.29
	SE x	0.45		0.41	0.55	9.19	1.09	16.59	25.86	0.74	8.44	0.32	0.40	5.63	2.13	0.21	0.06
	VW x	4.32	47.86	0.94	1.71	18.67	6.82	73.07	140.68	3.24	41.24	0.22	1.17	13.56	4.38	0.39	0.28
Bethal																	
5 events	VW x	4.36	43.65	0.00	1.09	0.50	13.74	75.16	152.05	3.45	28.05	2.49	5.11	0.85	6.65	0.33	0.45

event. Sulphate (n=16, $p<0.05$), ammonium ions and calcium (n=16, $p<0.01$) concentrations were inversely proportional to the duration of the event. Hydrogen ion loading (n=20, $p<0.01$) was shown proportional to volume.

The acidic anions were primarily sulphate and secondly nitrate. These were present in sufficiently large quantities to account for all the free acidity (Table 3.5). The multi-linear regression performed on the concentration data showed hydrogen ions dependant on sulphate, the duration of the event and calcium:

$$[H^+] = 2.21 \text{ Duration} + 7.83 [Ca^{++}] + 0.50 [SO_4^{=}] - 32.43$$

where $r = 0.99$

$p < 0.01$

$SE = 3.35$

The role played by the duration of the event may be related to the absorption of sulphur dioxide and its subsequent oxidation or, providing there is sufficient sulphate in the atmosphere, to the rainout of particulate sulphate.

3.3.2 Ermelo.

The site was located 5-10 km to the north-west of Ermelo on the farm Spitzkop. Nineteen events were sampled during the study period. These were similar in nature to those of Amersfoort, with an average duration of 7.3 hours, volume of 8.82 mm and intensity of 2.97 mm/hr. Most of the events occurred

Table 3.5 : The relative contribution by acidic anions to the volume weighted average pH of the precipitation samples (free acidity) collected in the eastern Transvaal Highveld during the study period. Each contribution is estimated from the ratio ($[X]/[H^+]$) of the volume weighted average concentration of the anion (μeq/l) and that of the hydrogen ions (μeq/l) as calculated from volume weighted average pH.

Element	$[X]/[H^+]$				
	Amersfoort	Ermelo	Morgenzon	Standerton	Bethal
Fluoride	0.01	0.03	0.03	0.02	0.00
Acetate	0.01	0.03	0.01	0.04	0.02
Formate	0.06	0.14	0.63	0.45	0.01
Chloride	0.09	0.14	0.17	0.14	0.31
Nitrate	0.81	1.23	1.07	1.55	1.71
Sulphate	2.02	2.19	2.53	2.98	3.46

at night and the wind in the upper air layers blew predominantly from the north-western or north-eastern sectors (Table 3.3).

The rain-water was usually acidic with pH values ranging between 3.81 and 6.56 units. The volume weighted pH was 4.23. The samples were characterized by high concentrations of sulphate (3.33-551.52 μeq/l; vol wt av=128.03 μeq/l), nitrate (1.77-284.65 μeq/l; vol wt av=71.68 μeq/l) and hydrogen ions (0.27-158.49 μeq/l; vol wt av=58.88 μeq/l). On occasions high values for ammonium ions (6.11-140.50 μeq/l; vol wt av=30.82 μeq/l) were recorded (Table 3.4). Very low concentrations of calcium, potassium, iron and manganese usually occurred. Fluoride, formate, potassium, calcium and magnesium were rarely deposited at this site.

The loadings of hydrogen ions, chloride, nitrate, sulphate, ammonium ions, potassium, iron and manganese ($n=19$, $p<0.01$) were proportional to the volume of rain that fell. The more rain, the higher the loading, implies an inexaustable supply of these species in the air mass and clouds during the event possibly due to nearby continuous sources such as Camden Power Station.

The free acidity of the rain water sampled could be accounted for by sulphate (Table 3.5). The second most important acidic anion was nitrate. The multi-linear regression equation related the concentration of hydrogen ions to nitrate, implying

that the site was too close to the access road and the machinary store. The equation was:

$$[H^+] = 0.44\,[NO_3^-] + 29.79$$

where $r = 0.72$

$p < 0.01$

$SE = 25.04$

3.3.3 Morgenzon.

The site in the Morgenzon district was located on the farm Rietvlei, 10-20 km to the south-west of the town. Most of the eleven rain events sampled occurred during the day. The average event lasted for 9.87 hours and the average volume and intensity was 9.16 mm and 4.16 mm/hr respectively. The wind (at 1000 m agl) usually blew from the north-western sector (Table 3.3).

The chemistry of the rain-water sampled at this site was characterized by sulphate (30.40-434.10 µeq/l; vol wt av=104.01 µeq/l), formate (0-467.90 µeq/l; vol wt av=61.36 µeq/l), nitrate (8.39-279.49 µeq/l; vol wt av=43.85 µeq/l) and hydrogen ions (14.45-117.49 µeq/l; vol wt av=40.74 µeq/l). The volume weighted pH was 4.39 with a range of 3.93 - 4.84 units (Table 3.4).

Hydrogen ion ($n=11$, $p<0.01$), chloride, nitrate, sulphate, sodium, ammonium ion, potassium, aluminium and iron

concentrations (n=10, $p<0.05$) and the loading of manganese (n=10, $p<0.05$) were inversely proportional to volume, implying that dilution of the samples occurred during rain events with a high volume. The concentration and loading of calcium and the loading of potassium (n=7, $p<0.05$) were proportional to the intensity of the storm. Neither the concentrations nor the loadings were related to the duration of the event.

Sulphate and, to a lesser extent, nitrate were the major acidic anions contributing to the free acidity of the rain water (Table 3.5). The multi-linear regression equation was:

$$[H^+] = 0.29\ [SO_4^=] + 13.51$$

where $r = 0.83$

$p < 0.01$

$SE = 9.14$

3.3.4 Standerton.

The site was located on the outskirts of the town. Most of the nine events occurred at night and the wind usually blew from the north-western sector on rain days. The average storm length was 9.70 hours, volume 10.4 mm and an average intensity of 3.94 mm/hr was calculated (Table 3.3).

The rain-water was acidic with pH values ranging between 4.00 and 4.86 units. The volume weighted average was 4.32 pH units. The major ionic constituents were sulphate (34.56-255.25 µeq/l; vol wt av=140.68 µeq/l), nitrate

(10.16-151.76 μeq/l; vol wt av=73.07 μeq/l), hydrogen ions (14.12-100.00 μeq/l; vol wt av=47.86 μeq/l) and ammonium ions (13.88-81.64 μeq/l; vol wt av=41.24 μeq/l) (Table 3.4). The loadings of fluoride, acetate, sodium, potassium, iron and manganese were reasonably constant during the entire study period. Very little calcium was deposited except during one event in March when an unusually large concentration was recorded.

The concentrations of the ions were not significantly proportional to the storm charateristics. The ecosystem loading of hydrogen ions, acetate, chloride, nitrate, sulphate and magnesium ($n=9$, $p<0.01$) were proportional to volume. Potassium ($\mu eq/m^2$) ($n=9$, $p<0.05$) was proportional to the intensity of the events.

The free acidity of the rain-water sampled at Standerton could be accounted for by sulphate and nitrate (Table 3.5). The multi-linear equation was:

$$[H^+] = 21.40\ [Na^+] - 7.75\ [Cl^-] + 29.64$$

where $r = 0.89$

$p < 0.01$

$SE = 11.28$

This result is surprising and cannot be easily explained. It is unlikely that the sodium and chloride originated from sea-salt and a local source of these pollutants is implied. The regression equation may also be misleading due to the large variability associated with rain data as a whole.

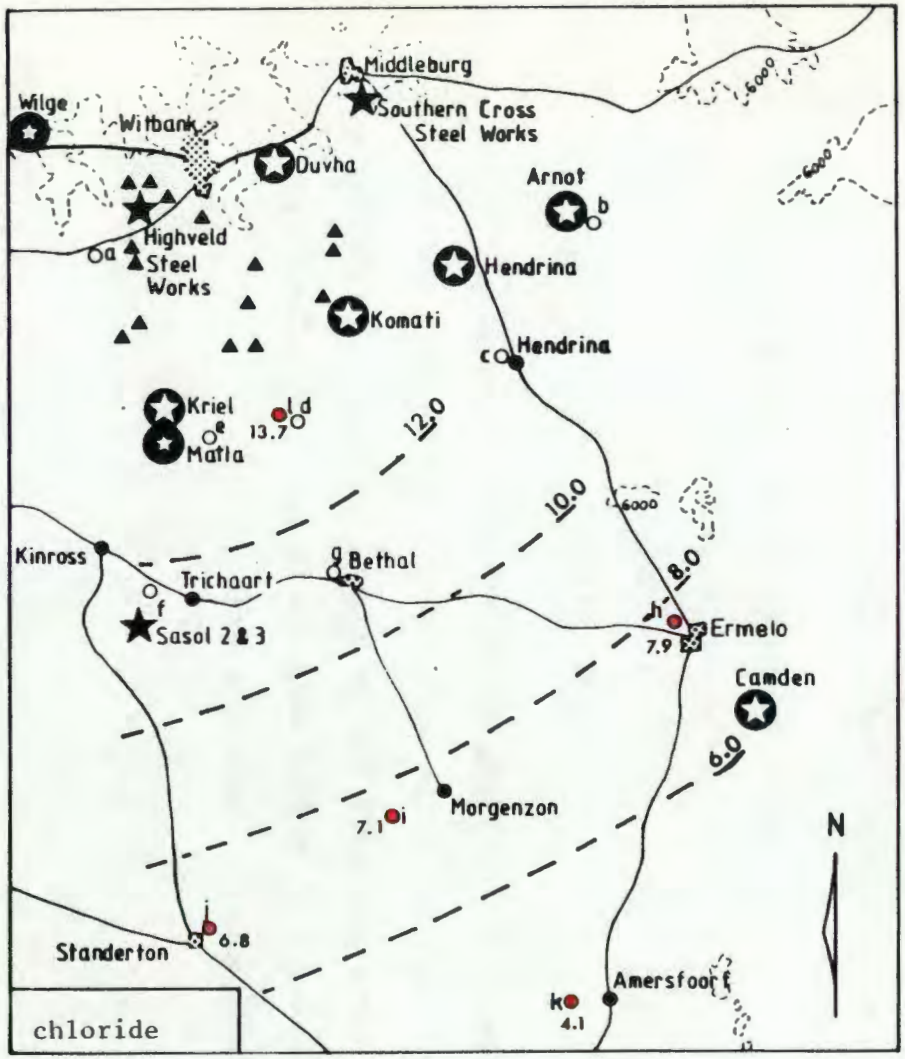


Figure 3.6: The spatial variations in the volume weighted average concentrations (μeq/l) of chloride wet-deposited in the eastern Transvaal Highveld.

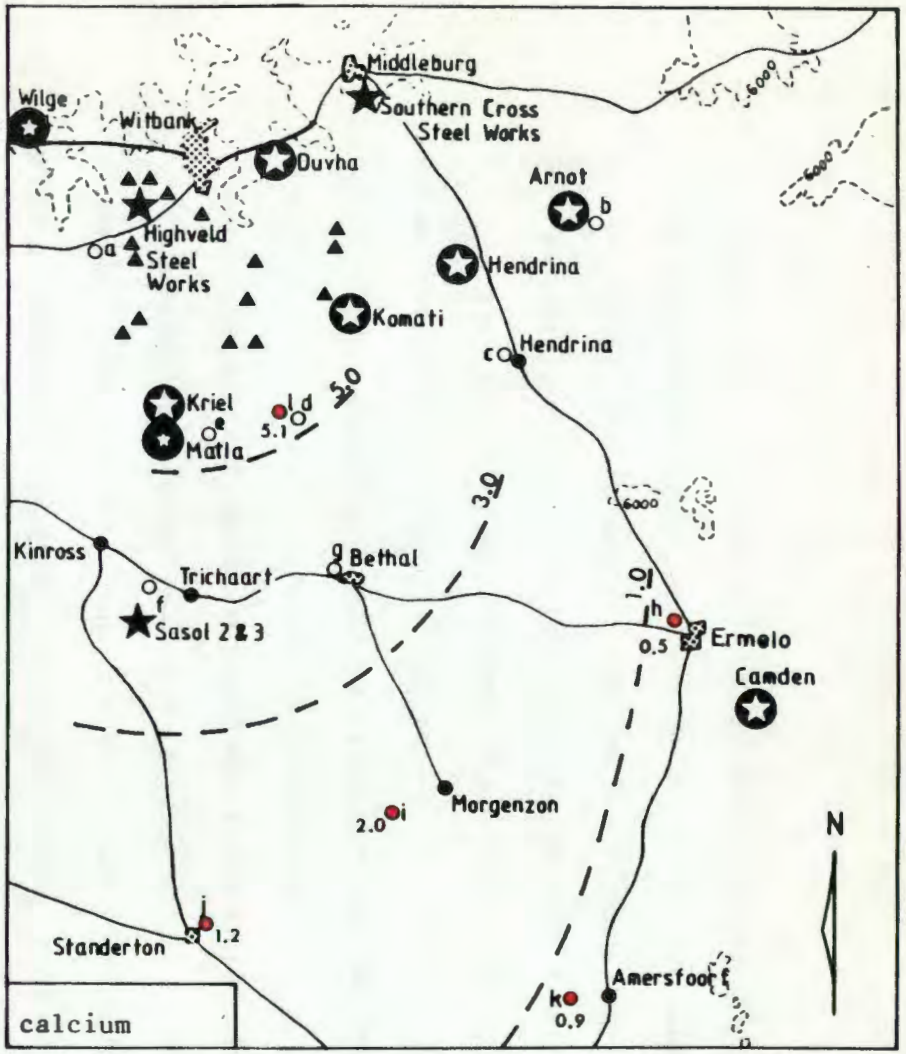


Figure 3.7: The spatial variations in the volume weighted average concentrations (μeq/l) of calcium wet-deposited in the eastern Transvaal Highveld.

3.3.5 Bethal.

This site was situated on the farm Boskraal at Elandsfontein, the only wet deposition site located within the bulk deposition network.

Unfortunately the storms were not sampled individually and although five samples were collected, the data could not be used for comparison purposes. The volume weighted averages were calculated and the major ionic constituents were probably sulphate, nitrate, ammonium ions and hydrogen ions. The volume weighted pH was 4.36 pH units (Table 3.4).

An analysis of the relative contribution of anions to free acidity using the volume weighted data implied that enough sulphate and nitrate were present to account for all the free hydrogen ions (Table 3.5).

3.3.6 Intersite Comparison.

The precipitation sampled at all of the sites was polluted and showed acidic tendencies. Mixtures of strong inorganic acids, primarily sulphuric and nitric, and neutralizing agents such as ammonium ions were the dominant ionic species. The Bethal site received the highest sulphate depositions on average and the volume weighted average pH value was higher than expected. This may have been due to the generally higher concentrations of cations recorded at this site. Ermelo received the most acid rain on average although Standerton recorded

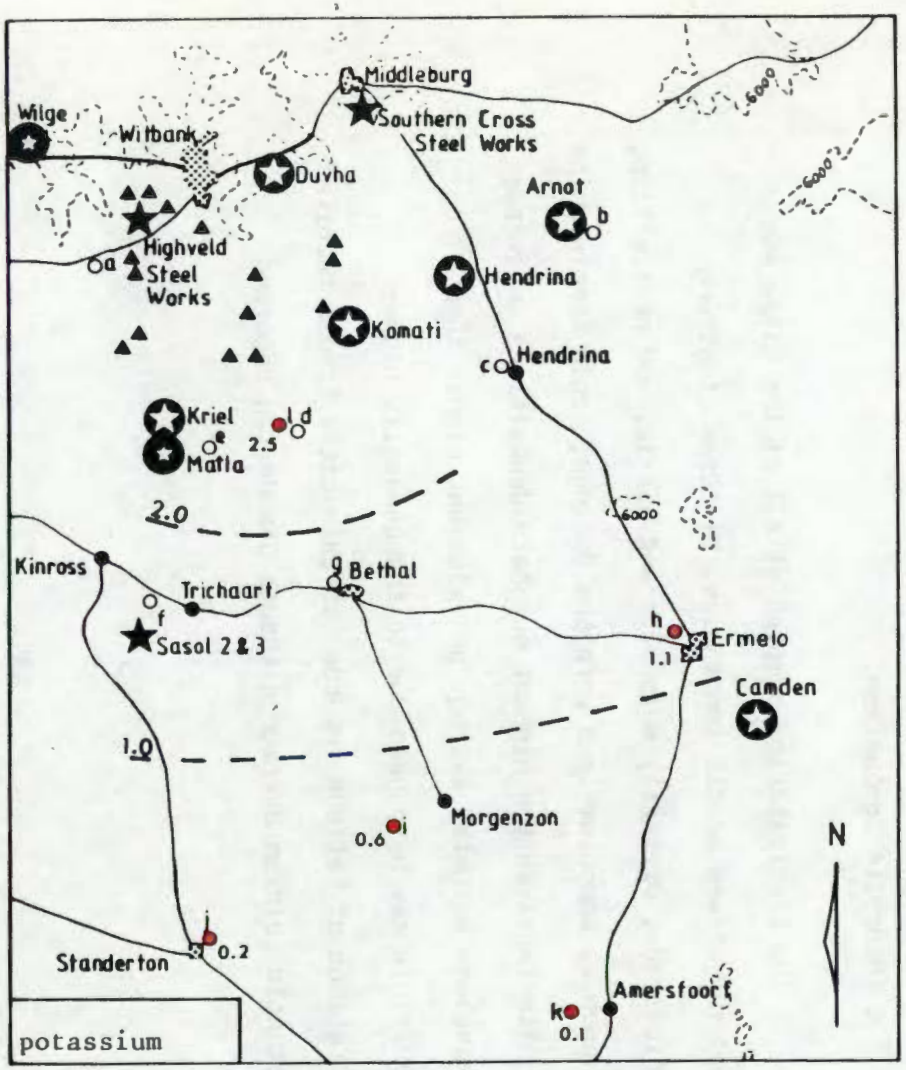


Figure 3.8: The spatial variations in the volume weighted average concentrations (μeq/l) of potassium wet-deposited in the eastern Transvaal Highveld.

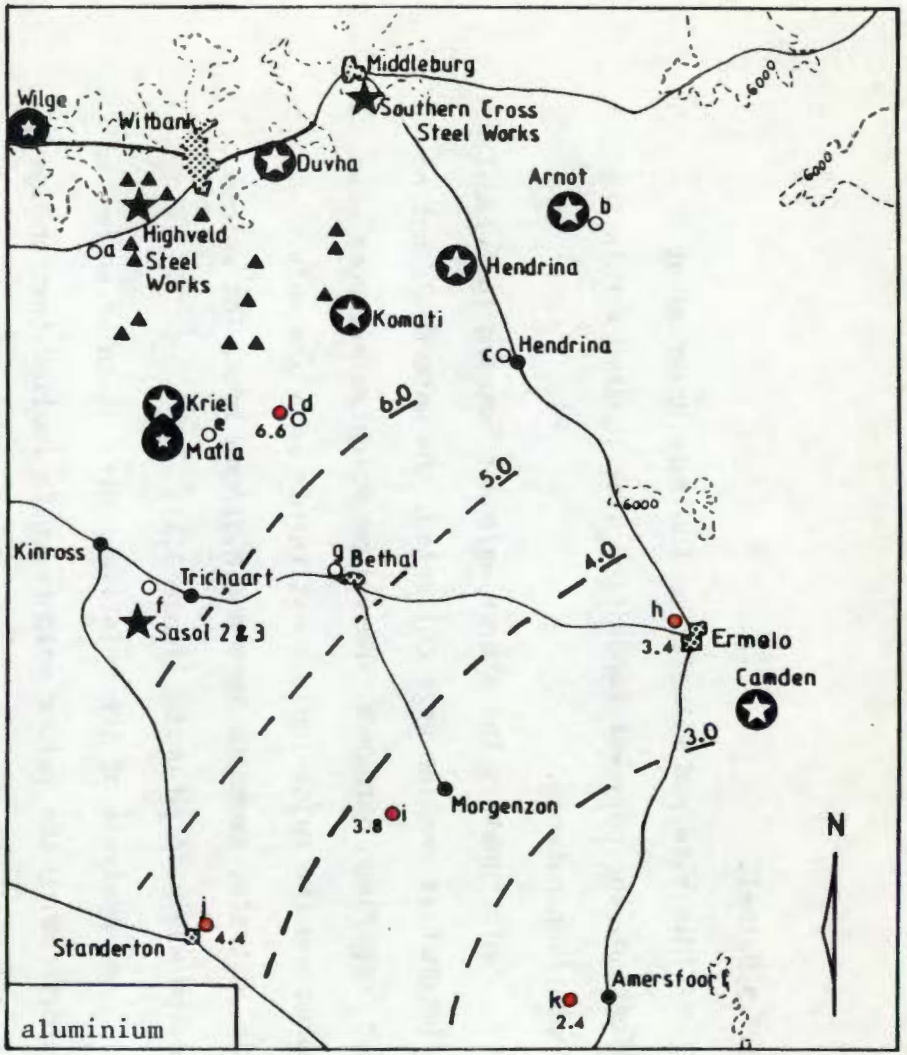


Figure 3.9: The spatial variations in the volume weighted average concentrations (μeq/l) of aluminium wet-deposited in the eastern Transvaal Highveld.

12 µeq/l more sulphate. The presence of an excess of 11.6 µeq/l of ammonium ions at Standerton over that recorded at Ermelo provides a feasible explanation.

The loadings of chloride, nitrate and sulphate recorded at Ermelo and Standerton increased with increasing rain volume whereas dilution effects were experienced at Amersfoort and Morgenzon. The wet deposition of these species at Ermelo and Standerton may have originated from local, continuous sources such as urban complexes, vehicular traffic and Camden Power Station. Such sources were distinctly absent in the regions around Morgenzon and Amersfoort.

The analyses of variance indicated no significant spatial variation in concentration or loading with the exception of chloride and calcium (Appendix 4.1). However, the areal deposition patterns of the volume weighted average concentrations do provide some information on the spatial variation of precipitation scavenging. Chloride, calcium, potassium and aluminium (Figures 3.6, 3.7, 3.8 and 3.9) exibit well defined spatial patterns with possible sources to the north and north-west of the study area. Maximum deposition of these species occurred at Bethal, close to the Witbank-Middleburg Power and Industrial Complex and the scavenging gradient decreased to the south-east. The wet deposition of manganese seemed to increase to the east (Figure 3.10). The trends exibited by nitrate,

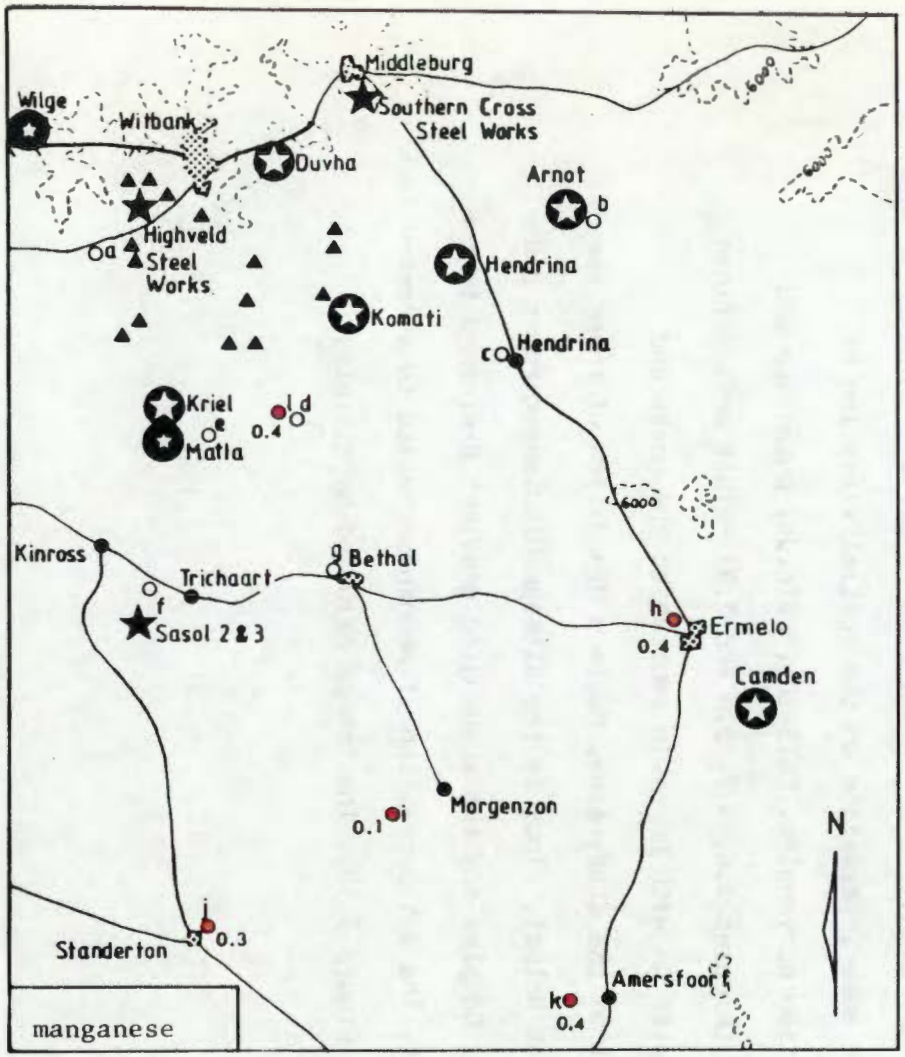


Figure 3.10: The spatial variations in the volume weighted average concentrations (μeq/l) of manganese wet-deposited in the eastern Transvaal Highveld.

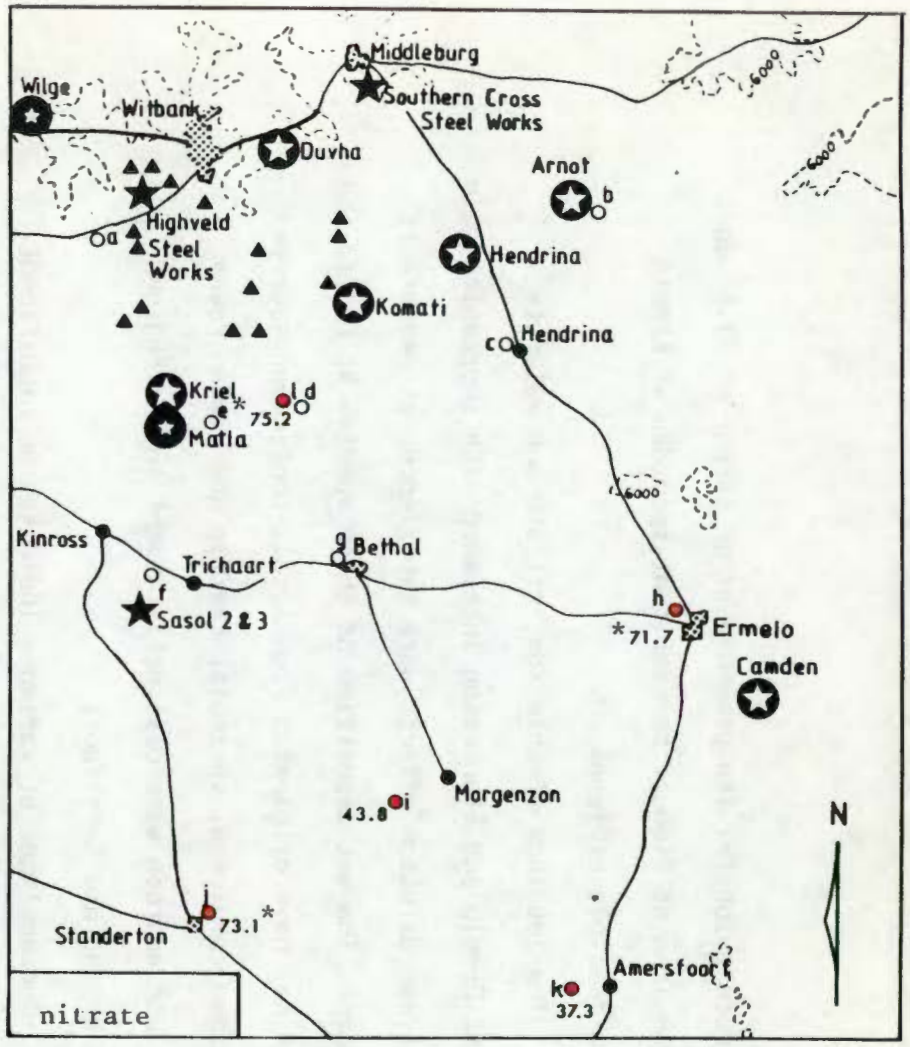


Figure 3.11: The spatial variations in the volume weighted average concentrations (μeq/l) of nitrate wet-deposited in the eastern Transvaal Highveld.

* The concentrations recorded at sites h, j and l may have been biased by vehicular traffic in the nearby vicinity of the samplers.

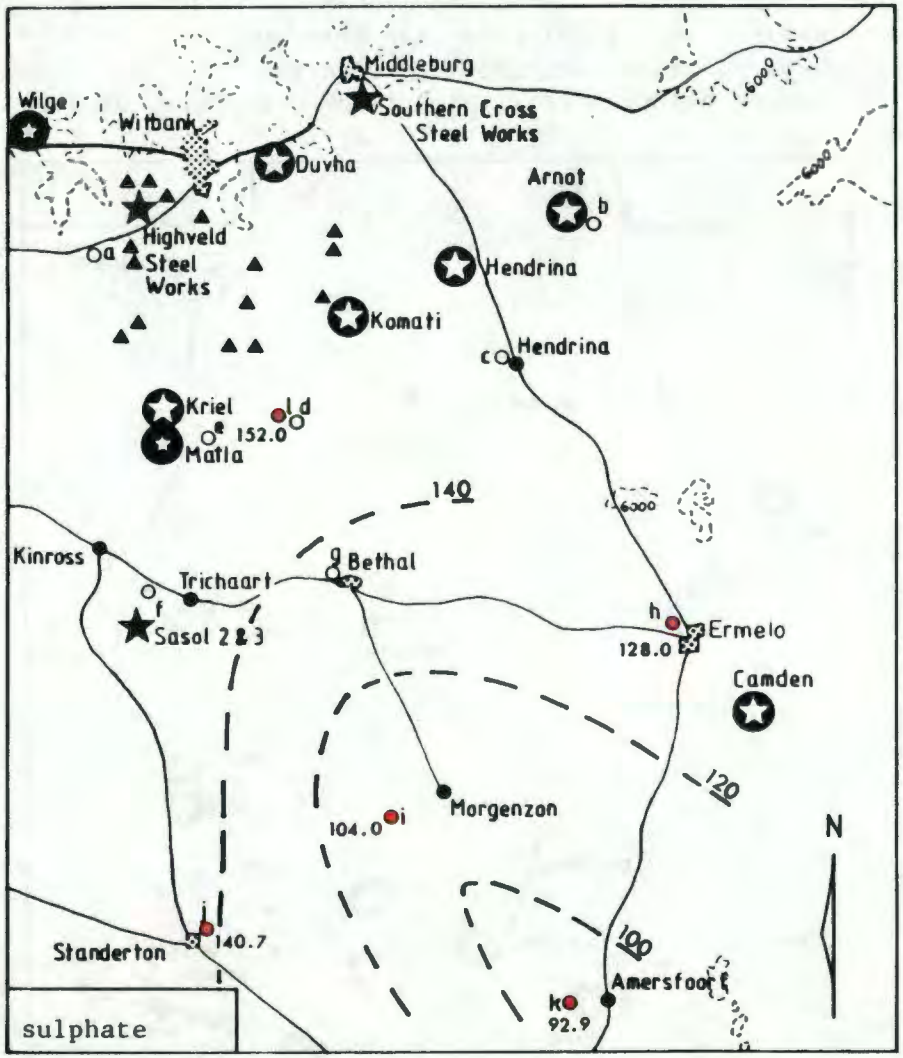


Figure 3.12: The spatial variations in the volume weighted average concentrations (μeq/l) of sulphate wet-deposited in the eastern Transvaal Highveld.

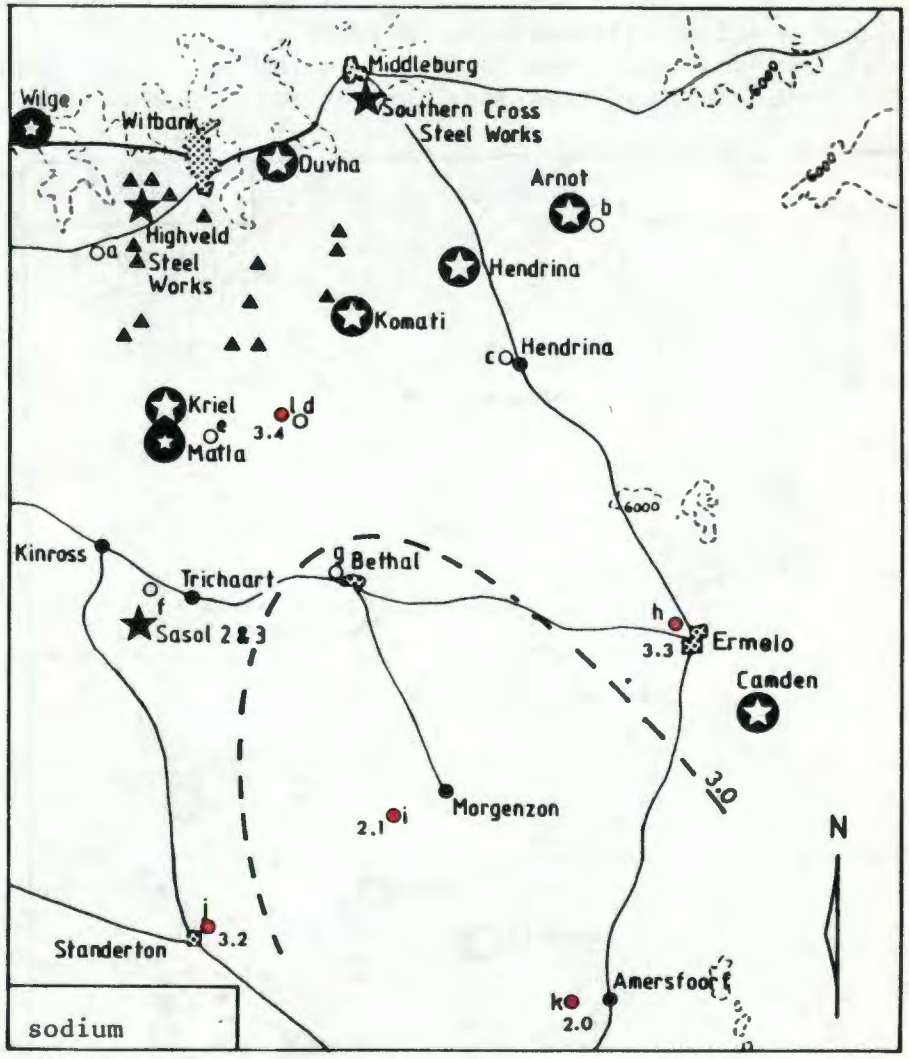


Figure 3.13: The spatial variations in the volume weighted average concentrations (μeq/l) of sodium wet-deposited in the eastern Transvaal Highveld.

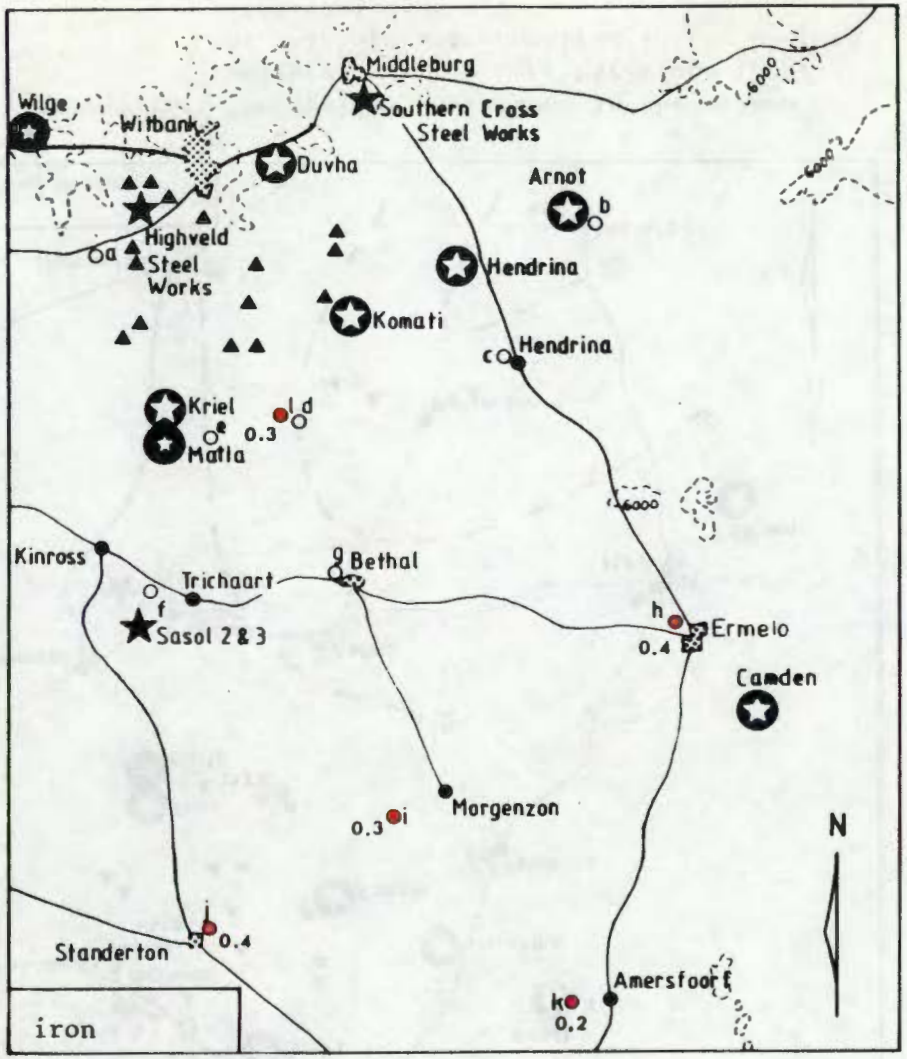


Figure 3.14: The spatial variations in the volume weighted average concentrations (μeq/l) of iron wet-deposited in the eastern Transvaal Highveld.

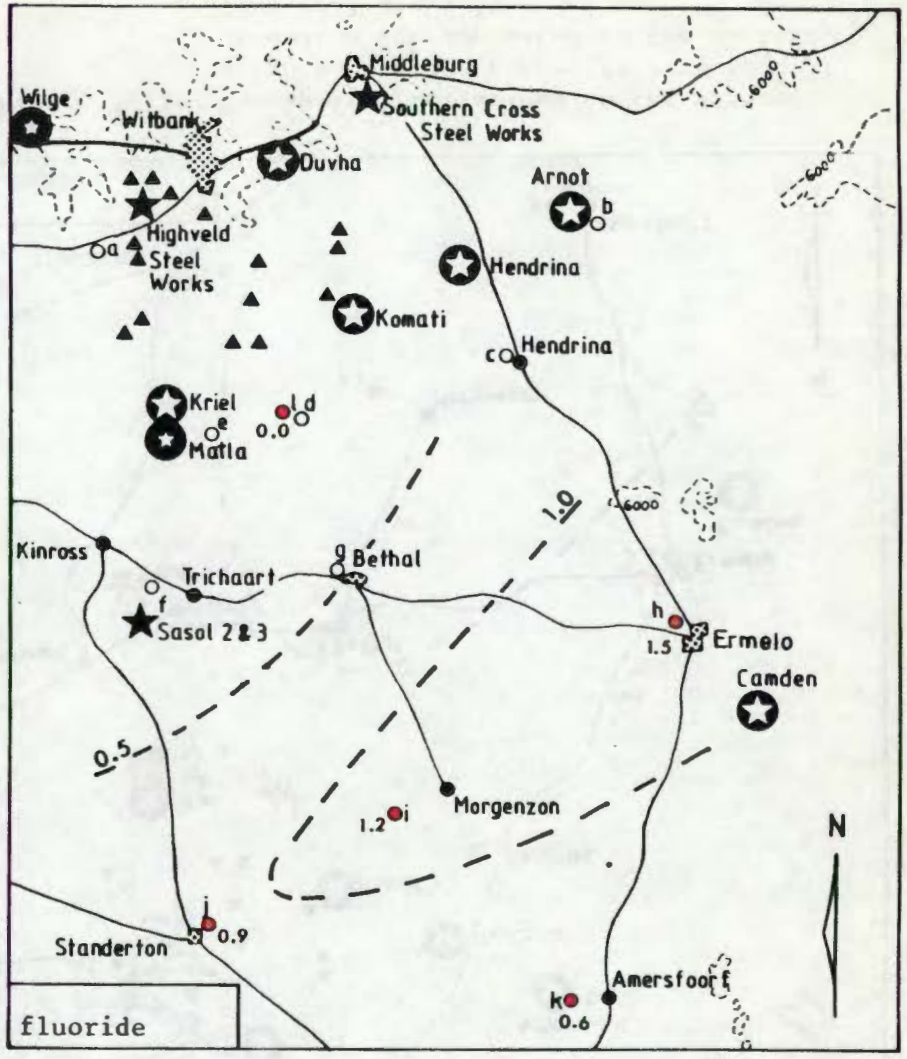


Figure 3.15: The spatial variations in the volume weighted average concentrations (μeq/l) of fluoride wet-deposited in the eastern Transvaal Highveld.

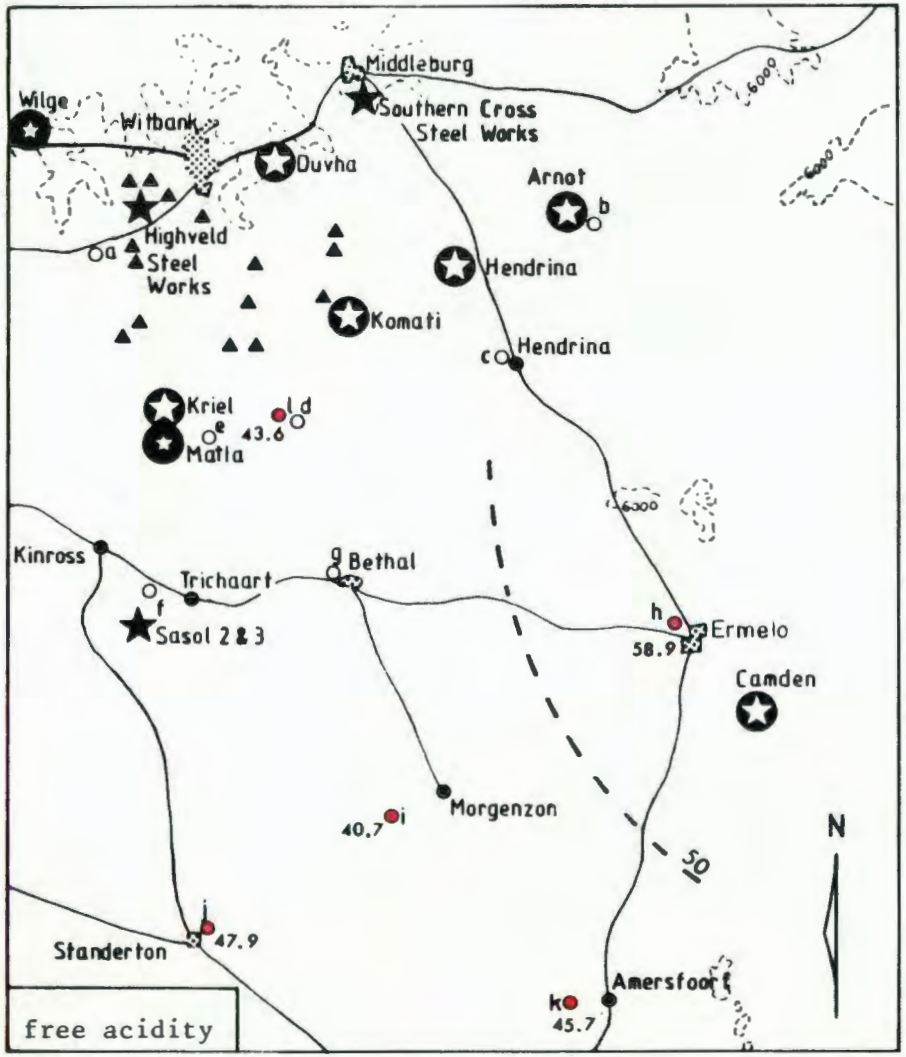


Figure 3.16: The spatial variations in the volume weighted average concentrations (μeq/l) of hydrogen ions wet-deposited in the eastern Transvaal Highveld.

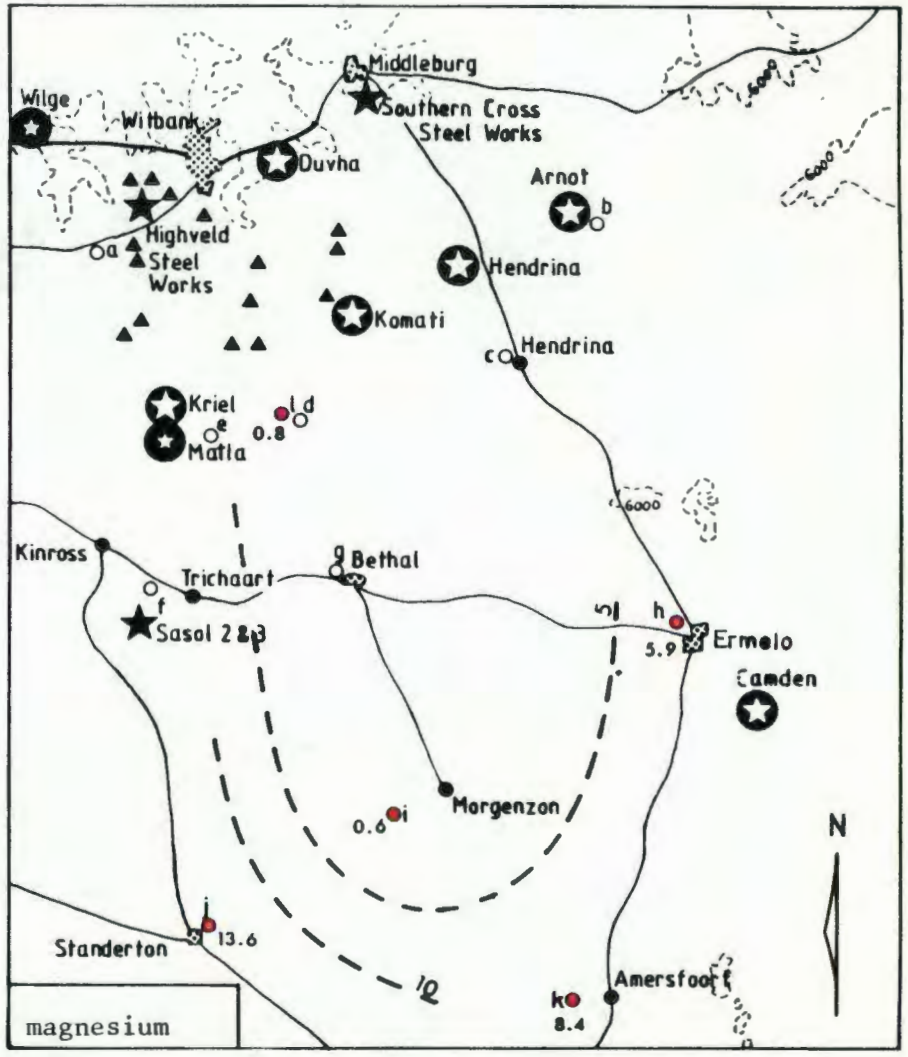


Figure 3.17: The spatial variations in the volume weighted average concentrations (μeq/l) of magnesium wet-deposited in the eastern Transvaal Highveld.

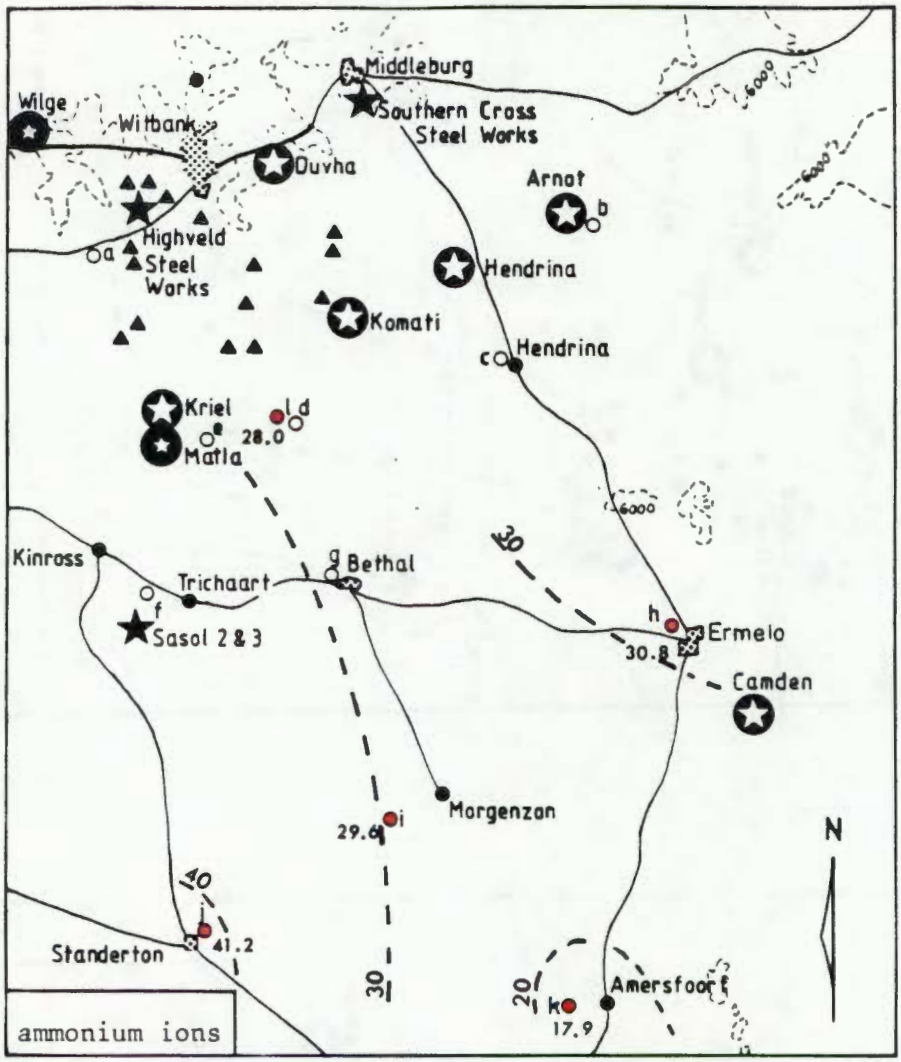


Figure 3.18: The spatial variations in the volume weighted average concentrations (μeq/l) of ammonium ions wet-deposited in the eastern Transvaal Highveld.

sulphate, sodium and iron were similar (Figures 3.11, 3.12, 3.13 and 3.14) but it is expected that sources of these species surround the study area from west to north to east (Figure 1.6). The deposition patterns were parabolic, possibly caused by the scavenging of local emissions at Standerton and Ermelo. The higher rates of nitrate deposition in the south may have been due to local vehicular traffic. The deposition of fluoride seemed to increase from the south-west to the north-east (Figure 3.15). The hydrogen ion and magnesium deposition increased from the north-west to the south-east and south (Figures 3.16 and 3.17). It is interesting to note that although the concentrations of all the major anions increased towards the north-west, hydrogen ion deposition increased to the south-east. The neutralizing effect of ammonium ions was possibly responsible for this. Standerton had the highest deposition of ammonium ions and Amersfoort the lowest (Figure 3.18). Thus although the sites to the north-west received more sulphate, there was also a greater potential for neutralization by ammonium ions.

The spatial trends in the wet deposition of formate and acetate were not considered because these organic acids are very unstable and since each event had a different exposure period, the deposition concentrations recorded are not comparable.

The events sampled during the study period were grouped into seven rain periods and the spatial and temporal variations in the rain water chemistry were investigated using

Table 3.6 : The duration, volume and intensity of the rain events and the upper air wind directions (extrapolated from Jan Smuts Airport, Johannesburg) during the extended wet period in March, 1984.

	Date	Duration (hours)	Volume (mm)	Intensity (mm/hr)	Wind Direction at 1000 m agl
Amersfoort	22 3 84	9.25	7.3	0.8	NNW
	22 3 84	19.00	7.1	0.4	NNW
	23 3 84	32.25	20.2	0.6	NNE
	24 3 84	13.00	17.3	1.3	NW
	25 3 84	8.00	19.0	2.4	NW
Ermelo	21 3 84	3.50	1.6	0.5	NW
	21 3 84	14.50	38.4	2.6	NW-NE
	22 3 84	5.50	12.3	2.2	NNW
	22 3 84	12.25	9.4	0.8	NE
	23 3 84	14.25	10.3	0.7	NNE
	24 3 84	6.25	2.1	0.3	NNW
	24 3 84	20.50	39.0	1.9	NNW
Morgenzon	22 3 84	13.00	12.7	1.0	NNW
	22 3 84	39.25	27.8	0.7	NNE-NNW
	25 3 84	16.00	22.6	1.4	NW
Standerton	21 3 84	34.50	29.8	0.9	NNE-NNW
	23 3 84	30.25	18.1	0.6	NNE-NNW
	24 3 84	0.50	5.7	11.5	NW
	25 3 84	5.50	7.2	1.3	NW

2X2 ANOVA and SNK tests. No spatial variations were detected. The results indicated that the concentrations of wet deposition did not vary significantly between the seven periods whereas the loadings of hydrogen ions ($p<0.01$), nitrate ($p<0.05$), sulphate ($p<0.01$), ammonium ions ($p<0.05$) and magnesium ($p<0.01$) recorded during the fourth period were significantly higher (Appendices 4.2 and 4.3). Upon closer inspection, this period received much more rain than the other periods and since hydrogen ions, nitrate, sulphate, ammonium ions and magnesium loadings exibited degrees of proportionality to volume, these results could be anticipated.

3.3.7 A Case of Wet Deposition Dynamics.

A week of wet weather was experienced by all the sites from 21 March, 1984. It rained almost continuously and several samples were collected. The trends in deposition during this period provide an interesting data base for studying deposition dynamics.

Five events were sampled at Amersfoort during this period (Table 3.6). These were separated by not more than five hours of no rain. The volume of rain recorded for each of these events was 7.35, 7.1, 20.2, 17.3, 19.0 mm respectively. Rain intensity was 0.8, 0.4, 0.6, 1.3, 2.4 mm/hr respectively.

The concentrations (μeq/l) of nitrate, sulphate and hydrogen ions decreased from the first to the third event, before

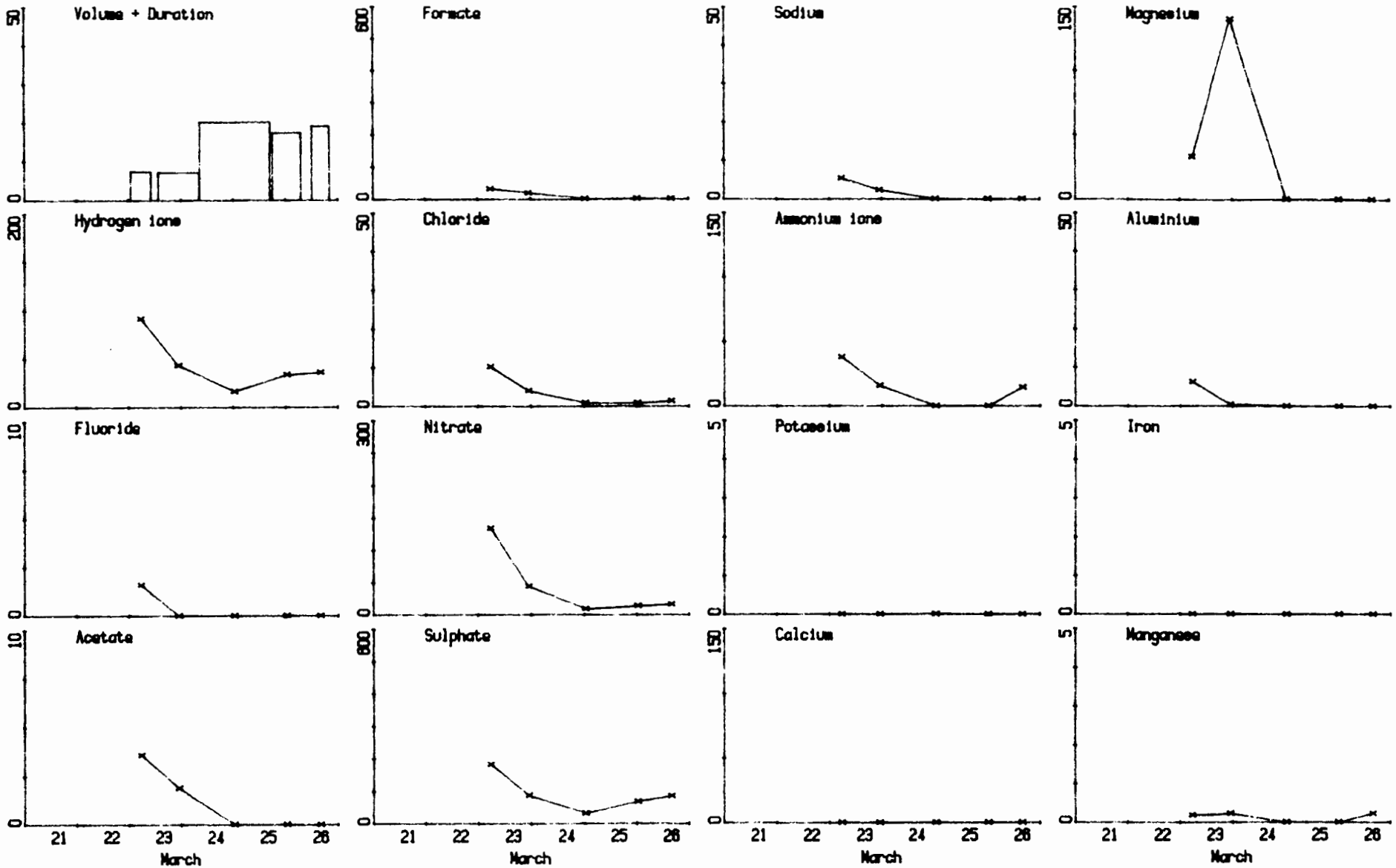


Figure 3.19 : The volume of rain (mm), and the concentrations (μeq/l) of the ions deposited during the extended wet period experienced at Amersfoort in March, 1984.

increasing again (Figure 3.19). Since the volume did not change much between the first two events, the decrease in concentration was most likely due to the rain washing the atmosphere clean. The very low concentrations recorded during the third event were probably related to both washing-out and dilution caused by the very high rain volume. Similar volumes were recorded for the fourth and fifth events but the concentrations of these ions increased noticably. Wind direction is suspected of causing the low concentrations. The wind direction during the third event was north-north-easterly in contrast to the north-westerly and north-north-westerly winds later.

A similar pattern occurred for the concentrations of chloride except that the deposition remained constant during the last four events. Since the volume of rain recorded in the second event was much lower than that of the last three events, it is suspected that these concentrations represent the background values of chloride in those air masses involved.

Fluoride, sodium, magnesium and aluminium were completely washed from the atmosphere by the first two events. The concentrations of manganese deposited remained constant. No potassium or calcium were deposited.

The site at Ermelo sampled seven events during this week of wet weather. These were separated by less than seven hours of no precipitation and were characterized by long periods of soft, penetrating rain (Table 3.6).

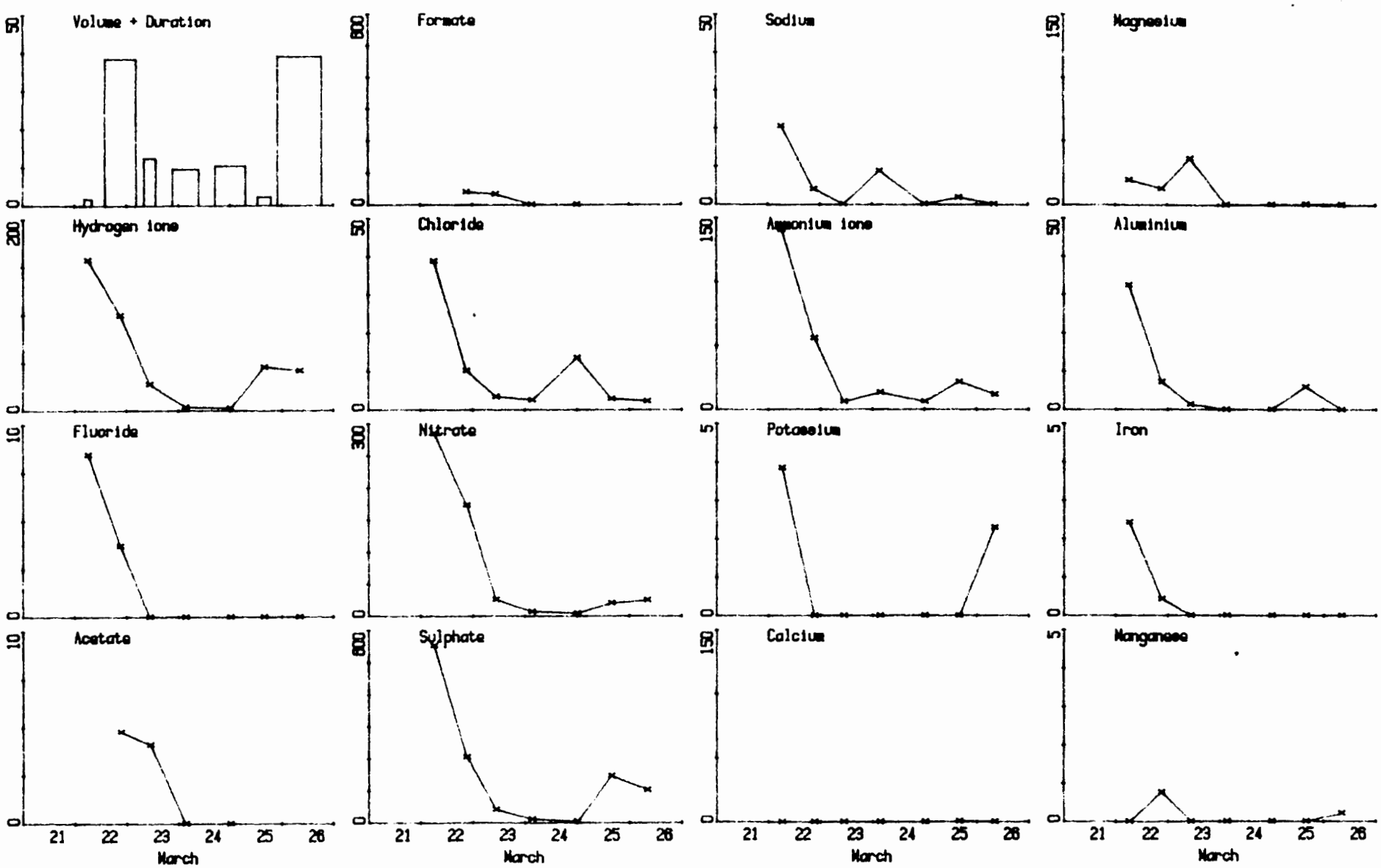


Figure 3.20 : The volume of rain (mm), and the concentrations (μeq/l) of the ions deposited during the extended wet period experienced at Ermelo in March, 1984.

The concentrations of aluminium and iron decreased as the wet period progressed (Figure 3.20). Since the volume of rain varied considerably, this was most likely not due to a dilution effect but rather to the washing of the atmosphere.

A similar trend occurred for nitrate, sulphate, ammonium and hydrogen ions, except for an increase in concentration during the last two periods. This was possibly due to the advection of polluted air from the Witbank/Middleburg Complex by the north-north-westerly winds.

The concentration of chloride deposited tended to a constant value except for a high during the fifth event. This increase was most likely due to the wind direction veering to the north-north-east. It is expected that the concentrations recorded were the background values for that particular period.

Three events were sampled at Morgenzon, the first two being separated by 3.25 hours of no precipitation and the second and third by fifteen hours. Possible wash-out and dilution are considered for the first two events only. The rain volume recorded during the second event was more than double that of the first event (Table 3.6).

The concentrations of chloride, nitrate, sulphate, sodium and hydrogen ions decreased as the period progressed (Figure 3.21). Considering the large volume difference this was most likely due to a dilution effect. Fluoride, acetate, formate, aluminium and iron were deposited during the first event only.

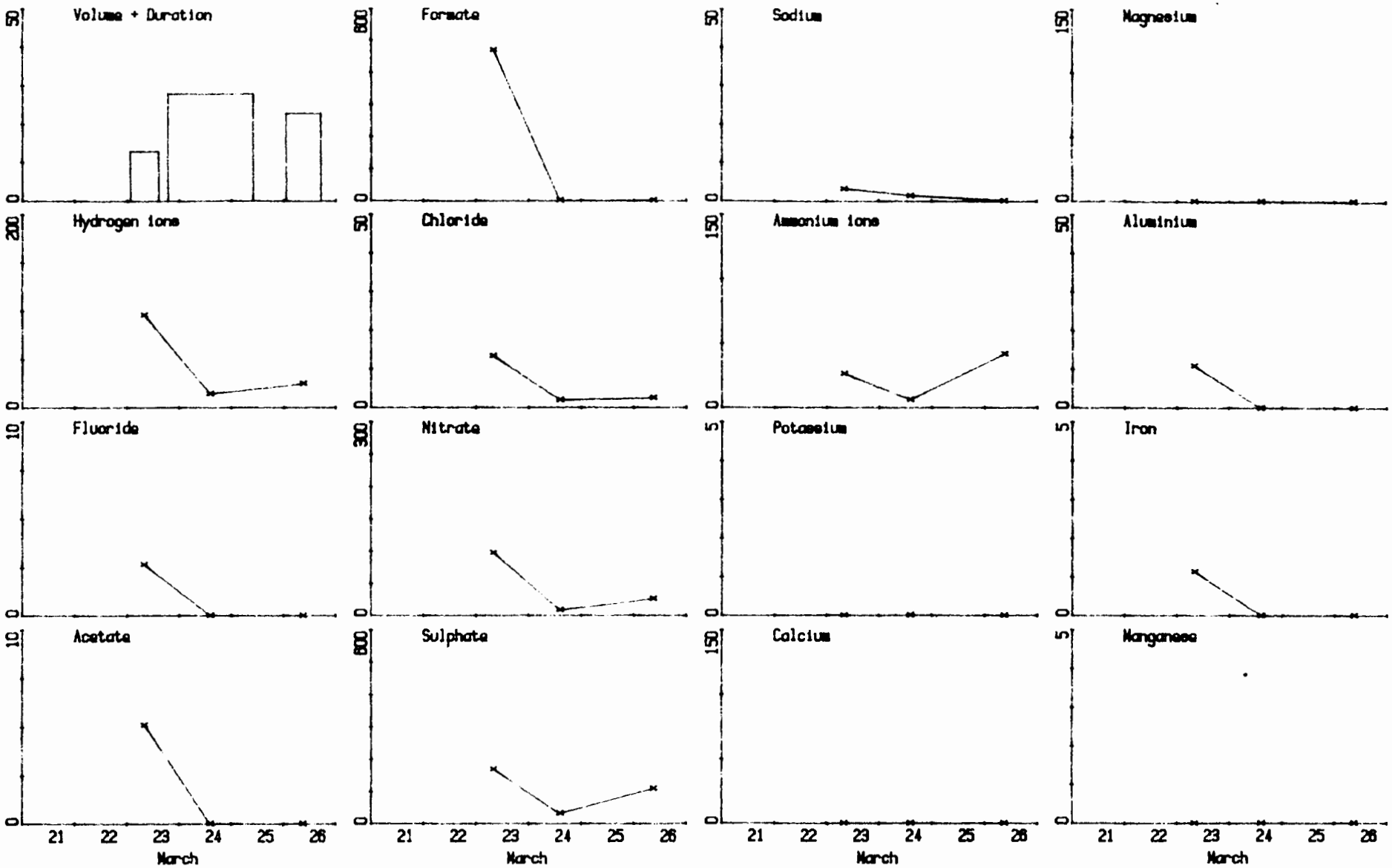


Figure 3.21 : The volume of rain (mm), and the concentrations (μeq/l) of the ions deposited during the extended wet period experienced at Morgenzon in March, 1984.

The deposition of chloride tended to a constant value during the second and third events despite the lengthy dry period and a change in wind direction. The volume and intensity of rain recorded for each of these events were similar. The values recorded could be due to dilution, but they closely resemble the background concentrations for Amersfoort and Ermelo and therefore it is suspected that these too are background concentrations characteristic of the air mass.

No potassium, calcium or magnesium was deposited during the wet period at Morgenzon.

Four events were sampled at Standerton during the wet period in March. The first two storms lasted for 34.5 and 30.25 hours respectively and were barely separated by a dry period. The third storm was very short and intense and after a delay of 12.5 hours, the fourth storm occurred. The dilution and washing effects during wet deposition are only considered for the first three events (Table 3.6).

The concentrations of manganese deposited and the volume of rain recorded decreased across the three events (Figure 3.22). The manganese was most likely washed from the atmosphere and not replaced during this period. The trends for nitrate, sulphate, magnesium and hydrogen ions show an initial high concentration with lows recorded for the second event and peaks in deposition during the third event. The concentrations recorded during the first event were most likely due to efficient removal processes whereas those of the third event were probably

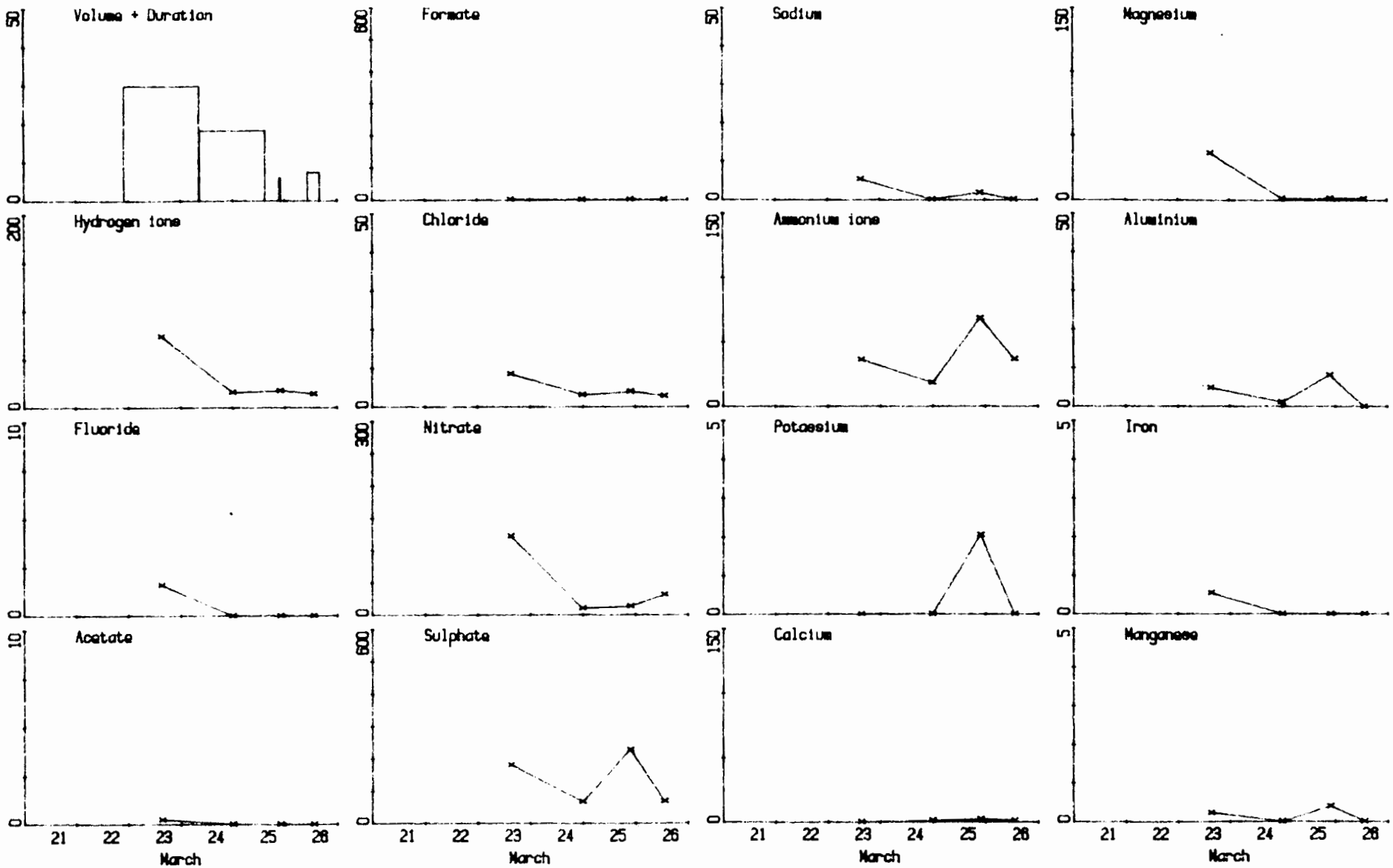


Figure 3.22 : The volume of rain (mm), and the concentrations (μeq/l) of the ions deposited during the extended wet period experienced at Standerton in March, 1984.

due to a concentrating effect related to the low volume of rain that fell.

Fluoride, acetate, formate and iron were deposited during the first event only. The concentrations of chloride again tended to a constant value similar to that recorded at the other sites.

3.4 DISCUSSION.

A brief study of the dynamics of wet deposition during an extended wet period has been presented. Acetate and formate were washed out completely during the first or second storm. Whether this was due to the complete removal from the atmosphere of these organic acids during the initial stages of the wet period, or due to total consumation by biota during the event is unfortunately unknown. Fluoride, sodium, potassium, calcium, aluminium and iron were absent in the rain samples collected towards the end of the wet period. This implies they were present in the atmosphere in finite quantities and if of local origins, production was severely limited during the rain events. Calcium, potassium and sodium are usually derived from soil particles and obviously wind erosion is hampered when the soil is wet. The origins of fluoride, aluminium and iron are most likely anthropogenic and their absence may have been related to wind

Table 3.7 : Volume weighted average concentrations (μeq/l) found in the rain water in other areas of South Africa.

Site	Description	pH	Concentrations in μeq/l								
			$[H^+]$	$[Cl^-]$	$[NO_3^-]$	$[SO_4^=]$	$[Na^+]$	$[NH_4^+]$	$[K^+]$	$[Ca^{++}]$	$[Mg^{++}]$
Mt Edgecombe[1]	North Natal coast			242.0			205.3		11.5	40.9	75.7
Zululand U.[1]	North Natal coast			235.2			221.0		8.2	43.9	70.4
Cedara[1]	80 km from Natal coast, rural			26.5			31.3		4.6	22.9	15.6
Ntabmhlope[1]	160 km from Natal coast, rural			4.8			7.4		3.1	13.5	5.8
Cathedral Pk[1]	200 km from Natal coast, rural			5.4			8.3		3.1	12.0	10.7
Punda Maria[2]	Northern Transvaal, rural	4.97	10.8	32.0	21.7	20.8	26.7	16.5	2.3	10.0	6.7

[1]Murgatroyd (1983)

[2]Dr. W.C. Keene, pers. comm (July, 1984).

direction. It is possible that these species were present, but in amounts too small for detection.

The concentrations of hydrogen ions, sulphate, nitrate and ammonium ions were variable during the wet period. Their deposition showed no tendency towards a background value nor were they totally removed from the atmosphere. Partial removal towards the end of the extended rain period may have occurred, but the lower concentrations were possibly due to dilution effects. Higher depositions were usually recorded when the wind blew from the north-western sectors. Sulphate, nitrate and ammonium ion concentrations in the rain water increased during and after these winds. These pollutants probably originated from this direction considering the density and nature of the industries to the north-west of the study area (Figure 1.6).

The data of three other studies on the chemistry of South African rain water are available (Table 3.7). A few storms were sampled at Punda Maria during the 1983/84 rain season. This site is situated in the northern Kruger National Park and is managed by the University of Virginia (USA) as part of their Global Precipitation Chemistry Network for monitoring the chemistry of rain water falling in remote areas of the world. They also manage a site at Cape Point but considering the differences in the rain formation mechanisms and the origins of

Table 3.8 : Volume weighted averages (μeq/l) of the ionic composition of precipitation recorded in other areas of the world.

Site	Description	pH	Volume weighted averages (μeq/l)								
			$[H^+]$	$[Cl^-]$	$[NO_3^-]$	$[SO_4^{=}]$	$[Na^+]$	$[NH_4^+]$	$[K^+]$	$[Ca^{++}]$	$[Mg^{++}]$
Amsterdam Island[1]	Remote Indian Oc	4.92	12	208	1.7	8.8	177	2.1	3.7	7.4	38.7
Poker Flat Alaska[1]	Remote	4.96	11	2.6	1.9	7.1	1.0	1.1	0.6	0.1	0.2
Katherine Australia[1]	Remote	4.78	16.6	11.8	4.3	5.5	7.0	2.0	0.9	2.5	2.0
San Carlos Venezuela[1]	Remote	4.81	15.5	2.5	2.6	2.7	1.8	2.3	0.8	0.3	0.5
Tewaukon Minnesota[2]	Remote	5.27	5.4	49.9	25.7	36.3	11.7	47.9	5.9	52.5	22.5
Itasca Minnesota[2]	Remote	5.00	10.0	46.8	20.0	31.9	8.7	33.6	4.4	34.5	19.2
Tovdal Norway[3]	Remote suspect LRT		~ 45	~ 27	~ 30	~ 70	~ 20	~ 30	~ 2	~ 15	~ 4
St Georges Bermuda[1]	Remote suspect LRT	4.79	16.2	175.0	5.5	18.3	147.0	3.8	4.3	9.7	34.5
Hovland Minnesota[2]	Remote suspect LRT	4.67	21.5	26.2	20.7	39.4	6.1	37.1	3.3	20.0	10.8
Lancaster NW England[4]	Rural small town		34.0	79.0	28.0	89.0	57.0	55.0	4.0	35.0	15.0
Pinard Canada[5]	Rural near Sudsbury	4.50	33.0		20.0	64.0					
Essex Canada[5]	Rural near Detroit	4.20	63.0		41.0	74.0					
Bowen P/S Georgia[6]	Rural polluted		31.6		8.3	33.2		10.9			
Toronto Canada[5]	Urban	4.10	84.0		55.0	96.0					
Florida USA[7]	Urban		29.5	27.6	13.6	42.7	19.1	7.1	5.1	20.5	10.0
Pasedena California[8]	Urban polluted		87.0	29.0	75.0	60.0	25.0	33.0	2.1	9.6	6.6
New York N Y State[9]	Urban polluted		119.0	43.4	39.1	125.2	35.8	11.2	2.4	16.1	12.8

[1]Galloway et al (1982)
[2]Munger (1982)
[3]Glover et al (1979)
[4]Harrison et al (1983)
[5]Melo (1981)
[6]Chen et al (1982)
[7]Hendrey et al (1980)
[8]Liljestrand et al (1978)
[9]Freely et al (1979)

the moist air, these data are not considered relevant. Punda Maria receives rain of a similar origin to that of the study area, except with less access to pollution. It can therefore be regarded as a background site.

The rain sampled at Punda Maria was much less acidic than that falling in the eastern Transvaal Highveld (Tables 3.4 and 3.7). If the sulphate and nitrate recorded at Punda Maria are regarded as background levels, 14-22% of the sulphate and 29-58% of the nitrate recorded in the study area may have natural origins. The depositions of soil-derived elements were, on average, higher at the background site, possibly due to the severe drought experienced in the region and associated wind erosion. The sea-salt derived elements deposited in the eastern Transvaal Highveld were similar to those recorded by Murgatroyd (1983) in the Natal Drakensberg.

The volume weighted average concentrations recorded during the study period were of a similar magnitude to those measured in large urban and industrial complexes overseas (Table 3.8). The pH values were similar to those of Essex, Toronto, New York City and Pasedena. Nitrate values at Standerton, Bethal and Ermelo compared with those of the Los Angeles Basin, a disturbing result considering the photochemical smog problems experienced in that region and the role of nitrate in its formation. The origins of the nitrate deposited at these three sites were most likely localized (possibly due to vehicular traffic) since Amersfoort and Morgenzon recorded much lower concentrations.

Table 3.9 : The annual wet deposition of Sulphate (kg/Ha/yr) recorded in other areas of the world.

Site	Description	Deposition (kg/Ha/yr)
Indiana/Wisconsin[1]	Industrial	140-160
Brookhaven Nat. Lab., USA[2]		30.9
North America[3]	Heavy Industrial	1-30
Europe[3]	Heavy Industrial	20-40
North America[3]	Rural	1-20
Europe[3]	Rural	2-20
Alabama/Arkansas[1]		3.7
North Atlantic[3]	Ocean	1-3
Remote Oceans[3]	Ocean	0.1-0.2
Remote Continental[3]	Remote	0.1-5.0

[1]Evans et al (1981) [2]Raynor et al (1982)
[3]Record (1981)

The amounts of sulphate wet-deposited in the study area were large by global standards, similar to those of Toronto and New York City. If the annual deposition (kg/Ha/yr) is considered, the eastern Transvaal Highveld may receive loadings equivalent to those of the highly industrialized regions of Europe (Tables 3.9 and 3.10).

The chemical quality of the rain water sampled in the eastern Transvaal Highveld is disturbing when it is considered that a standard of 25 μeq/l of hydrogen ions (or a pH of 4.60 units) has been suggested as a necessary step towards the abatement of acidic precipitation (Evans et al, 1981). This value relates to the free acidity requirements of forest ecosystems and the acidity threshold which, when exceeded, causes permanent lake acidification in sensitive areas. A loading threshold of 20 kg/Ha/yr has been suggested for sulphate following research on the levels associated with ecological damage (NACA, 1984). The deposition of hydrogen ions and the estimated annual loading of sulphate in the eastern Transvaal Highveld exceed both these limits by a factor of two (Tables 3.4 and 3.10).

The study area is chiefly agricultural and the free acidity introduced through precipitation is probably small in comparison to the contributions by agricultural activities and natural processes (Krug et al, 1983). The amount of nitrogen required by crops has been estimated at 100-300 kg/Ha/yr, although this is dependant on the crop (Evans et al, 1981). The amounts of sulphate utilized by plants varies greatly but values

Table 3.10 : The potential annual wet depositions (kg/Ha/yr) of the fourteen ions at the four study sites in the eastern Transvaal Highveld. The depositions were calculated from the average rain volume for each area (as supplied by the South African Weather Bureau) and the volume weighted averages (μeq/l) as calculated from the data collected during the study period.

	Potential annual wet deposition (kg/Ha/yr)			
	Amersfoort	Ermelo	Morgenzon	Standerton
Av annual rain vol (mm)	689.3	777.5	677.4	719.3
Fluoride	0.1	0.2	0.1	0.1
Acetate	0.6	1.4	0.3	0.7
Formate	2.2	5.8	20.1	6.0
Chloride	1.0	2.2	1.7	1.7
Nitrate	15.9	34.6	18.9	32.6
Sulphate	30.8	47.8	34.6	48.6
Sodium	0.3	0.6	0.3	0.5
Ammonium ions	0.6	1.4	0.3	0.7
Potassium	0.0	0.3	0.2	0.0
Calcium	0.1	0.1	0.3	0.1
Magnesium	0.7	0.6	0.0	1.2
Aluminium	0.1	0.2	0.2	0.3
Iron	0.0	0.1	0.0	0.0
Manganese	0.1	0.1	0.0	0.0

of 13 kg/Ha/yr for rice to 96 kg/Ha/yr for sugar cane have been reported (Evans et al, 1981). An estimate of 18.5 kg/Ha/yr for maize and wheat crops has been suggested. Tabatabai et al (1976) showed, for example, that the 13-17 kg/Ha of Sulphur deposited over Iowa by precipitation played an important role in crop production.

It is unlikely that the eastern Transvaal Highveld is ecologically sensitive to acid precipitation. However, the projected annual wet depositions of hydrogen ions and sulphate exceed even those beneficial to European and North American agricultural ecosystems. The soils in the eastern Transvaal Highveld are sulphur deficient and may benefit from the higher depositions recorded. Should the wind blow the pollution from the Witbank-Middleburg Complex towards the north-east, similar depositions could occur in the forests of the eastern Transvaal, a potentially sensitive area. If the results of overseas research on the ecological damage to forests by excessive quantities of sulphate and hydrogen ions can be applied to the South African situation, there is sufficient reason to be concerned about the ecological future of this area.

3.5 SUMMARY.

The precipitation sampled at all of the sites was polluted and showed acidic tendencies. All the free acidity could be accounted for by sulphate and nitrate. No spatial variations in wet deposition were statistically significant except for chloride and calcium. The spatial patterns of the volume weighted averages indicated an increase in the deposition of acidic ions towards the source area whereas the free acidity of the rain increased to the east and south-east, away from the Witbank-Middleburg Power and Industrial Complex. The lower acidity levels experienced close to the source area were most likely related to the distribution of neutralizing species such as ammonium ions. Temporal variations were due to the effects of volume on ecosystem loading.

A brief examination of deposition during an extended period of rain, showed complete washout of the soil-derived species, fluoride, aluminium and iron during the initial storms after which no deposition was recorded. The deposition of chloride tended to a constant value at all the sites, implying the existence of a background level possibly related to the origin of the air mass. Sulphate, nitrate, ammonium ions and hydrogen ion depositions showed some sign of diminishing as the wet period progressed, possibly related to wind direction, dilution effects and washing of the atmosphere. Replenishment of

these species occurred rapidly during brief dry periods and when the wind blew from the north western sectors.

When compared to the wet deposition recorded elsewhere in South Africa, the eastern Transvaal Highveld received significantly larger depositions of anthropogenically derived species. On a global scale, the depositions of sulphate, nitrate and hydrogen ions corresponded to those measured in highly industrialized and urbanized areas of Europe and North America. Soil-derived species were deposited in quantities similar to those recorded at rural continental sites.

The study area was located in a basically rural and agricultural region. The amounts of sulphate and hydrogen ions deposited exceeded those levels recommended for agricultural areas in the United States. The levels recommeded for sensitive areas in Europe and North America were also exceeded. Should these levels be applicable to the South African situation, there is sufficient reason to be concerned about the quality of rain water in the study area, and the future of any ecologically sensitive areas downwind of the Witbank-Middleburg Industrial Complex.

CHAPTER 4.

CONCLUSIONS.

This study focussed on the chemistry and severity of atmospheric depositions in the eastern Transvaal Highveld. These were examined in a regional context, in and around the Witbank-Middleburg Power and Industrial Complex.

Bulk depositions were considered initially. These were sampled using deposit gauges because, despite the criticisms levelled at this technique, no alternative methods are suitable for routine monitoring on a regional scale.

The conclusions of the research on bulk depositions are:

1. that the chemical compositions of the bulk depositions were dominated by acidic ions such as sulphate (94-214 kg/Ha/yr), chloride (20-59 kg/Ha/yr) and nitrate (12-28 kg/Ha/yr) and by soil derived species such as calcium (17-52 kg/Ha/yr).

2. that the annual deposition rates for sulphate and nitrate are in the same quantitative order as those of highly industrialized areas in Europe and North America, where rates of 20-250 kg/Ha/yr for sulphate and 20-30 kg/Ha/yr for nitrate have been recorded.

3. that the surface winds from the southern, south-western and south-eastern sectors were related to lower bulk depositions at most sites whereas northerly, north-westerly and north-easterly winds correlated to higher depositions. The Witbank-Middleburg Power and Industrial Complex lies to the north and north west of the study area and sulphur, chlorine and nitrogen compounds are emitted by the power stations and/or heavy industries. It appears that the acidic ions deposited originated from these complexes.

4. that on a regional scale there was little spatial variation in the annual deposition rates of most of the species considered and the study area was possibly covered by a chemically homogeneous layer of smog. It appears that sulphate and chloride were deposited in greater amounts closer to the pollution source-area but this trend may have been due to the limitations of the sampling technique chosen.

5. that despite the expected increase in the bulk depositions during the summer months due to an added input from wet removal processes, the bulk deposition rates of most of the species considered were apparently uninfluenced by season of year. Therefore it appears that dry removal processes play an important role in the deposition of atmospheric material in the study area.

6. that the deposition rates recorded at the site closest to a power station stack (Arnot) were significantly higher and more irregular than elsewhere. The higher deposition rates for sulphate and chloride may be attributed to gaseous absorption during plume looping episodes.

The high depositions of acidic ions measured during the bulk deposition study led to the establishment of a wet deposition network further to the south-east of the Witbank-Middleburg Power and Industrial Complex. The sampling techniques chosen were modified from those recommended following research on the change in pH with time after the end of the rain event and pH was measured in the field as soon after the end of the storm as possible.

The conclusions of the research on wet depositions are:

1. that the rain water samples were acidic with volume weighted average pH values that ranged between 4.23 and 4.39 units. The lowest pH measured occurred during a storm sampled at Amersfoort on 10 March, 1984. This rain event lasted for half an hour during which 2 mm of rain fell and a pH of 3.72 was recorded.

2. that the chemical compositions of the rain were dominated by acidic ions such as sulphate (volume weighted averages of 92-152 μeq/l), nitrate (37-75 μeq/l) and hydrogen ions (40-59 μeq/l) and neutralizing agents such as ammonium ions (17-41 μeq/l).

3. that the wet depositions of sulphate, nitrate and hydrogen ions appear to be much larger than those recorded in other areas of South Africa. Average values of 21 μeq/l for sulphate, 22 μeq/l for nitrate and 11 μeq/l for hydrogen ions have been measured in the northern Transvaal.

4. that the volume weighted average concentrations (μeq/l) for sulphate, nitrate, hydrogen and ammonium ions are in the same quantitative order as those of heavily industrialized and urbanized areas of Europe and North America, where concentrations of 60-125 μeq/l of sulphate, 20-75 μeq/l of nitrate, 30-119 μeq/l of hydrogen ions and 10-55 μeq/l of ammonium ions have been recorded.

5. that the free acidity of the wet depositions can be attributed to sulphate and nitrate. Since the origins of atmospheric sulphur in this area are entirely anthropogenic and although the origins of nitrate are less certain, the rain water falling in the eastern Transvaal Highveld can be described as polluted.

6. that higher concentrations of sulphate, nitrate, hydrogen and ammonium ions were recorded in the rain water when the wind (1000 m agl) blew from the north western and northern sectors. Although the pollution from Camden Power Station in the east may have played a role, it appears that most of the acidic ions deposited in the rain originated from the Witbank-Middleburg Power and Industrial Complex.

7. that there were no significant spatial variations in the wet deposition rates and the study area could be considered to be covered by a chemically homogeneous smog.

8. that the average wet deposition rates of the acidic species increased slightly towards the north and north west (that is towards the pollution source-area) whereas the free acidity of the rain increased slightly to the east and south-east and with distance from the Witbank-Middleburg Power and Industrial Complex. The higher quantities of ammonium ions deposited in the rain water sampled to the north and west of the study area were probably responsible for neutralizing some of the acidic ions deposited closer to the source-area. Thus although the free acidity levels were lower in the north and west of the study area, the rain falling was more polluted. This emphasizes the

need for the complete chemical speciation of rain water samples so that the origins of the free acidity and the potential for ecological interference can be accurately determined.

9. that the estimated annual wet deposition rates for sulphate (30-48 kg/Ha/yr) and the volume weighted average pH values (4.23-4.39) for the eastern Transvaal Highveld exceed the limits recommended for sensitive ecosystems (pH of 4.60 units and 20 kg/Ha/yr of sulphate) and the levels considered beneficial to agricultural systems (13-18 kg/Ha/yr of sulphate to grain crops).

The annual bulk and wet deposition rates can be compared to determine the relative roles played by wet and dry removal processes. In the bulk deposition study, the deposition rates of most of the elements considered were similar throughout the year despite the seasonal rain patterns characteristic of the area. The annual wet depositions of soil derived species and those related to industrial particulates such as fly ash were relatively small, implying a major contribution by dry removal processes. About half of the sulphate deposited annually may be attributed to dry deposition. Therefore, it can be concluded that the removal of atmospheric pollutants by dry deposition processes is important and should be seriously considered in future monitoring networks in the eastern Transvaal Highveld. Since the deposit gauge does not sample the dry deposition of small

particles realistically and the rates of sulphate and chloride deposition may be over-estimated, the use of this technique is not recommended.

The eastern Transvaal Highveld, a largely rural and agricultural region, is subjected to acid depositions comparable in magnitude to those of the heavily industrialized centres of Europe and North America. If the deposition rates and the associated ecological damage recorded in other areas of the world are considered as guidelines, there is sufficient reason to be concerned about the ecological future of the eastern Transvaal Highveld as a whole and in particular, of the sensitive areas downwind of the Witbank-Middleburg Power and Industrial Complex.

APPENDIX 1 : List of abbreviations, symbols and conversion factors.

A. Chemical Concentrations.

mg/l - milli-grams of species per litre.
mass per unit volume.

μeq/l - micro-equivalents of ion per litre of water, used for direct comparisons between the quantities of ions present in a unit volume.
$\mu eq/l = mg/l * C/MW * 1000$
where C : charge on the ion.
MW: molecular weight of the ion.

B. Ecosystem Loading.

mg/m^2 - milli-grams of species deposited per square metre.
mass per unit area.

$\mu eq/m^2$ - micro-equivalents of ions deposited per unit area.

C. Deposition Rates.

Tg/yr - teragrams of species deposited on the earth per year.
$Tg = 10^{12}$ grams
$= 10^{6}$ metric tons

$mg/m^2/day$ - mass deposited per unit area per day.

kg/Ha/yr - kilograms deposited per hectare per year.

D. Statistical Symbols and abbreviations.

vol wt av - volume weighted average, used to describe the mass or equivalents of ions deposited per unit volume of rain for the sampling period.
- volume weighted average concentration
vol wt av $[X] = \frac{\sum [X_i] / Vol_i}{\sum Vol_i}$
where [X]: ionic concentration in μeq/l.
Vol: rain volume in mm.
- vol wt av pH = $-\log_{10}$ (vol wted av $[H^+]$)
where $[H^+]$: hydrogen ion concentration in eq/l.

SE x - standard error of the mean.

n - number of datum points used in the analysis.

p - confidence level.

r - regression coefficient

E. Miscellaneous.

$\mu S/cm^2$ - unit of conductivity.
micro-Siemens per square centimetre.

m - metre.

m agl - metres above ground level.

pH - a measure of the free acidity of a solution.
$pH = -\log_{10}[H^+]$, where $[H^+]$ is in eq/l.

mm - volume of rain, one mm of rain is equivalent to one litre of water over an area of one square metre.

mm/hr - rain intensity.

APPENDIX 2 : The bulk deposition rates ($mg/m^2/day$) for the ions measured (Figures 2.2 to 2.12).

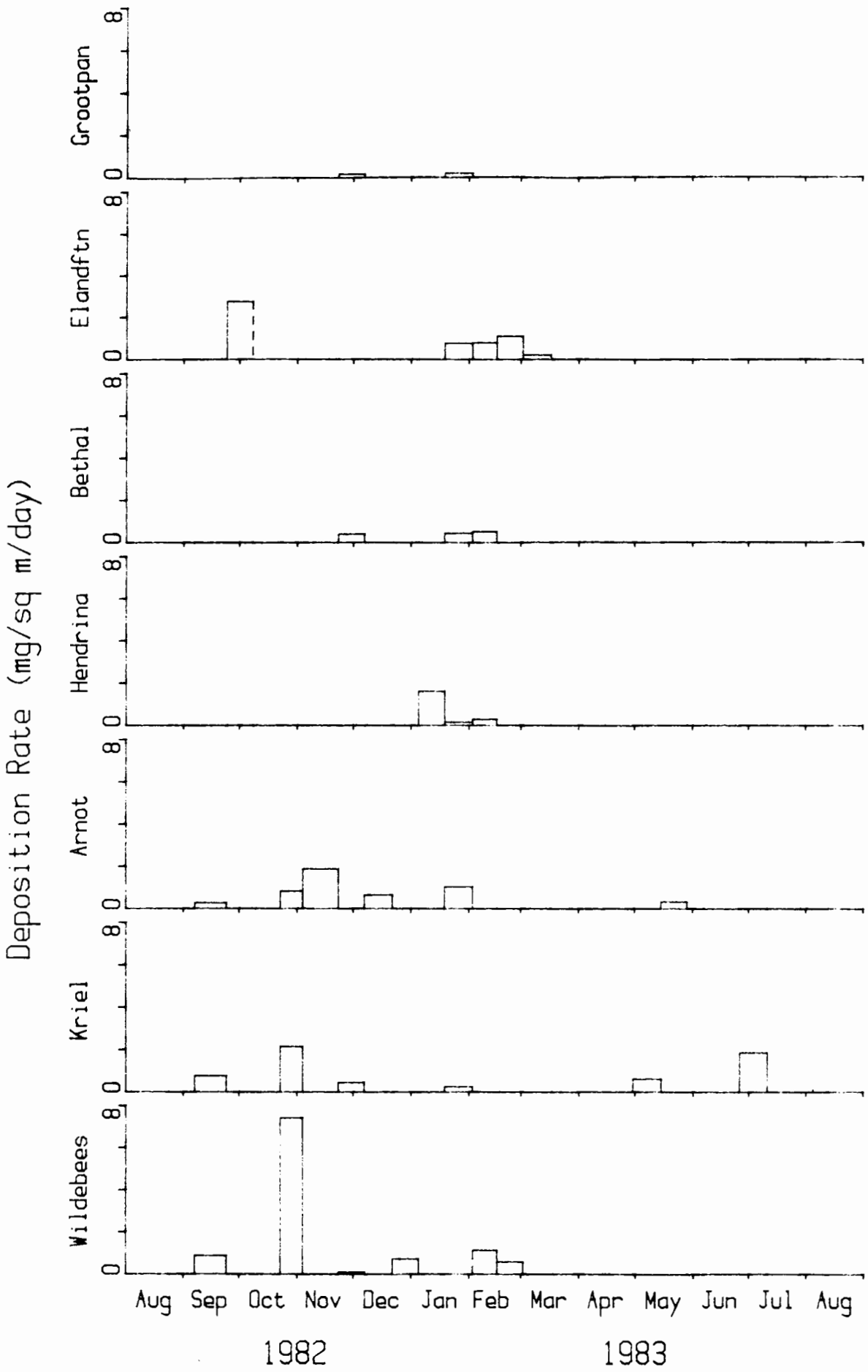


Figure 2.2 : Bulk Deposition rates in mg/sq m/day for Fluoride.

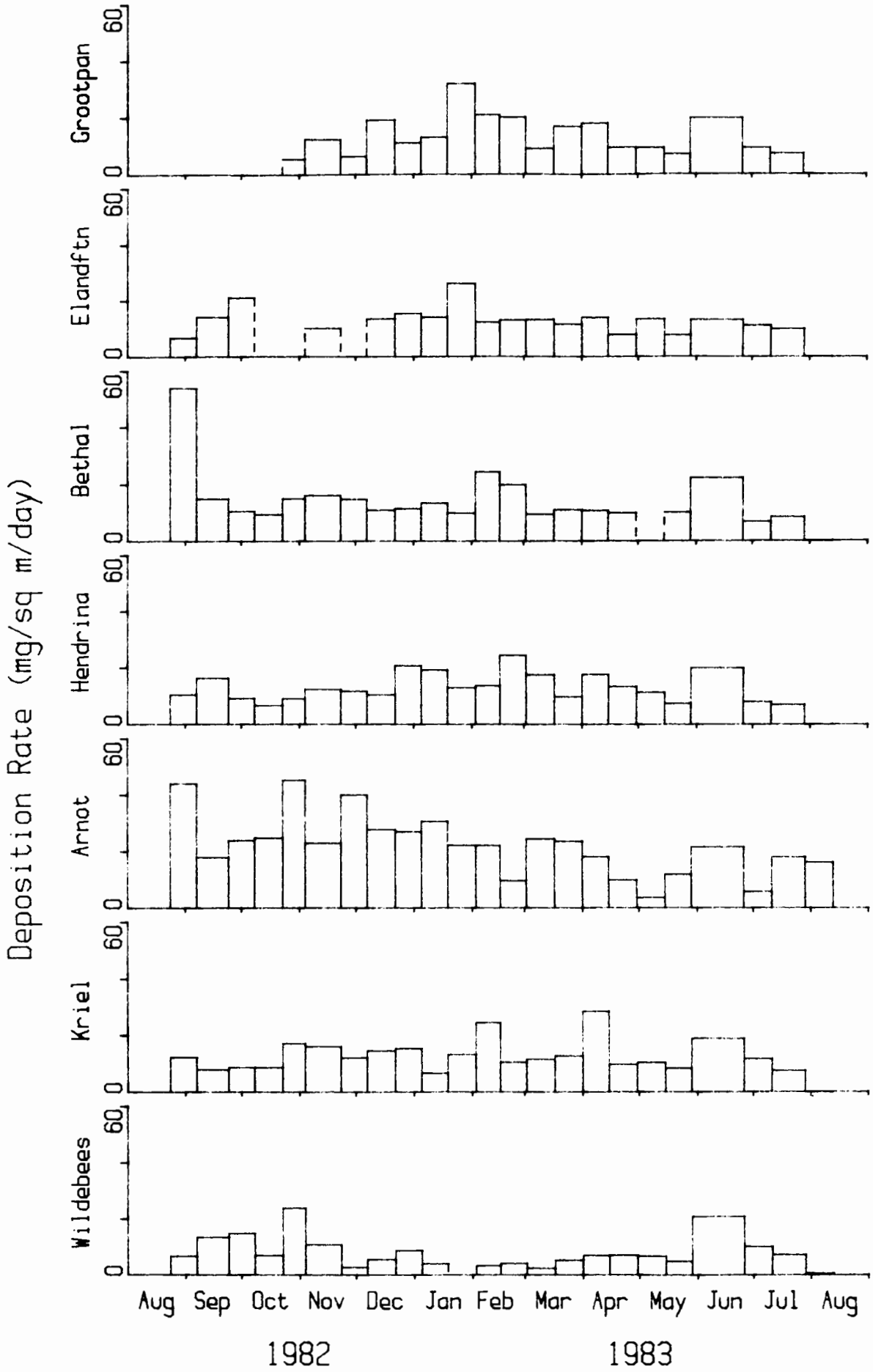


Figure 2.3 : Bulk Deposition rates in mg/sq m/day for Chloride.

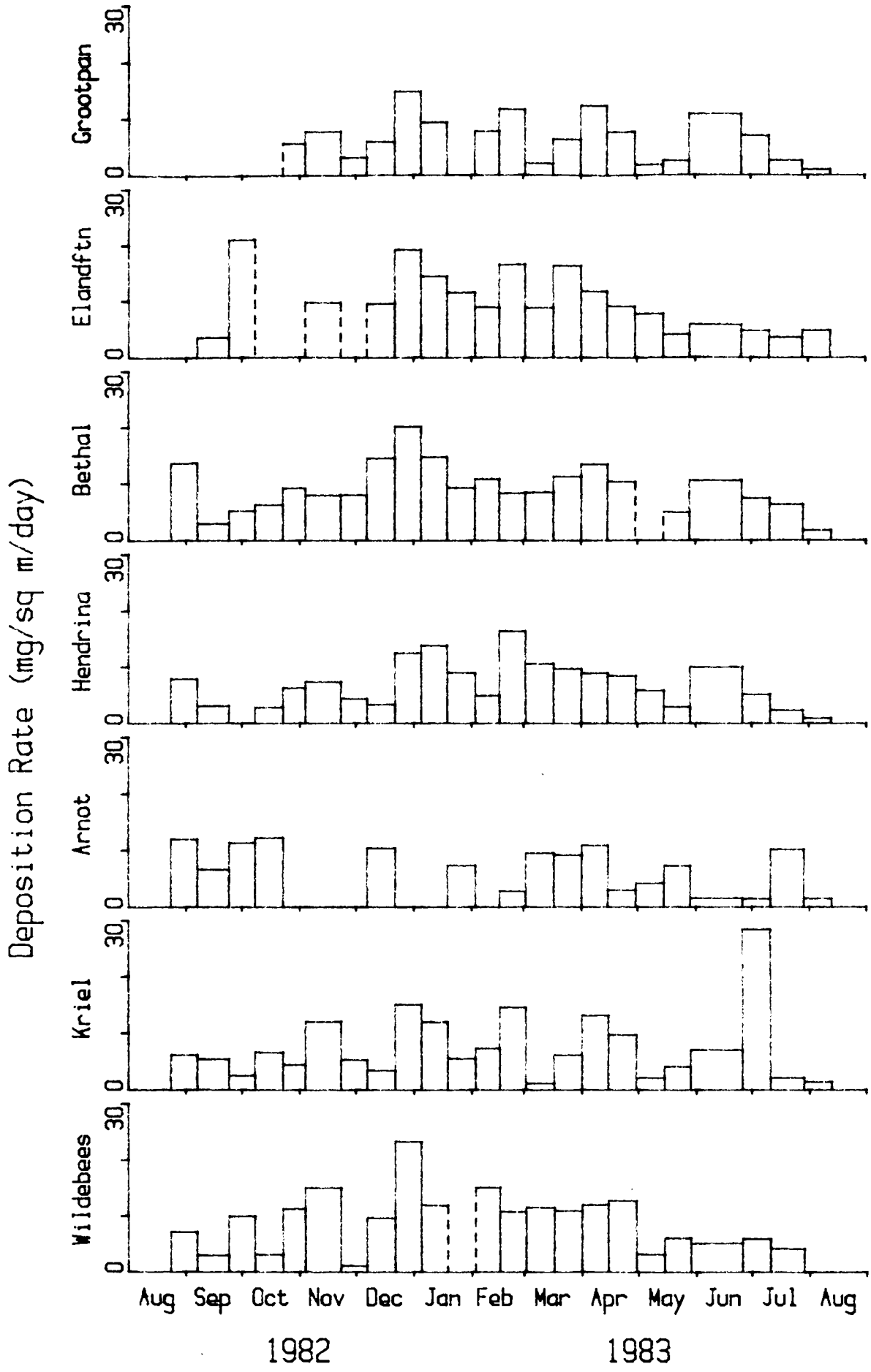


Figure 2.4 : Bulk Deposition rates in mg/sq m/day for Nitrate.

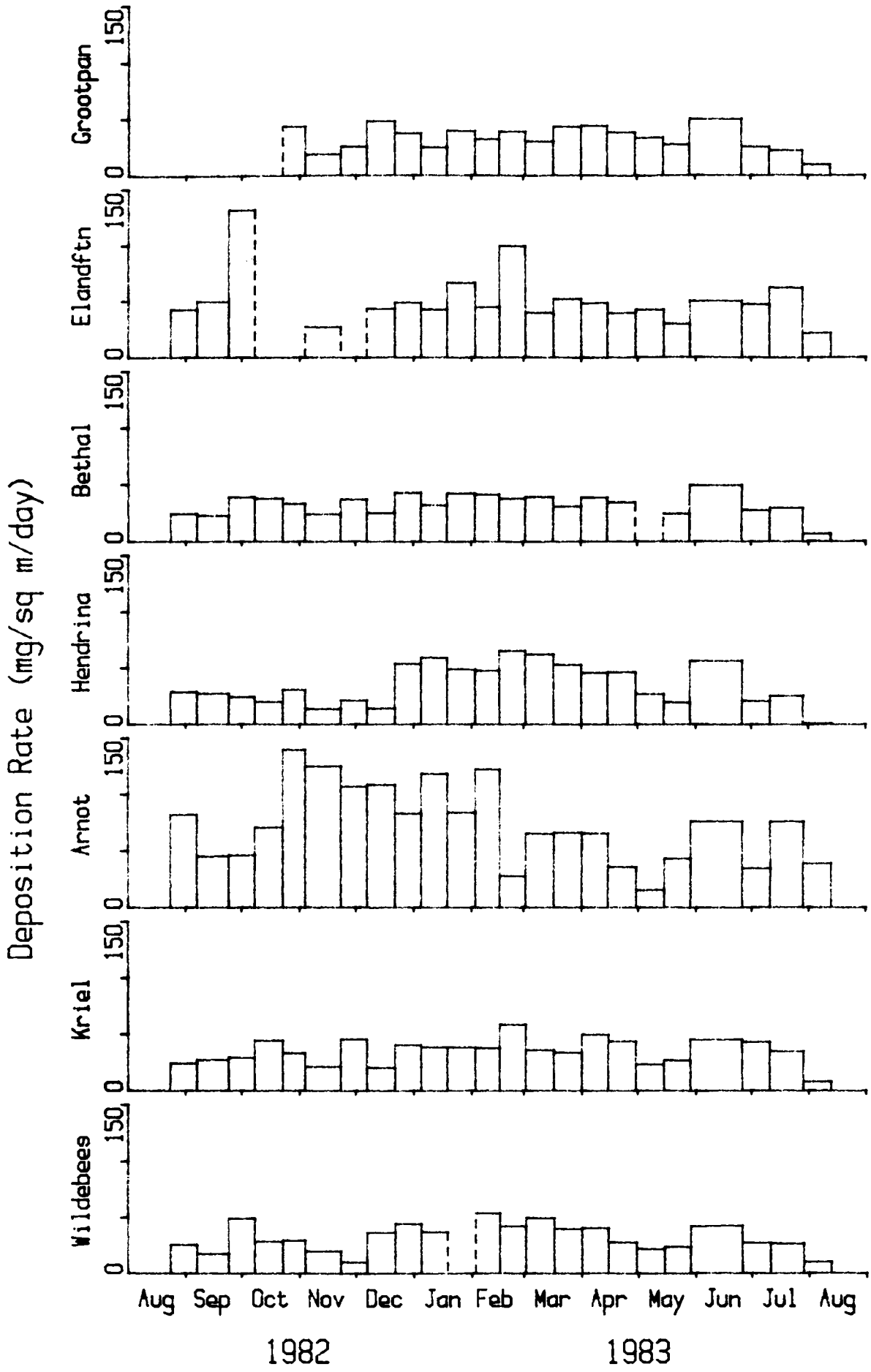


Figure 2.5 : Bulk Deposition rates in mg/sq m/day for Sulphate.

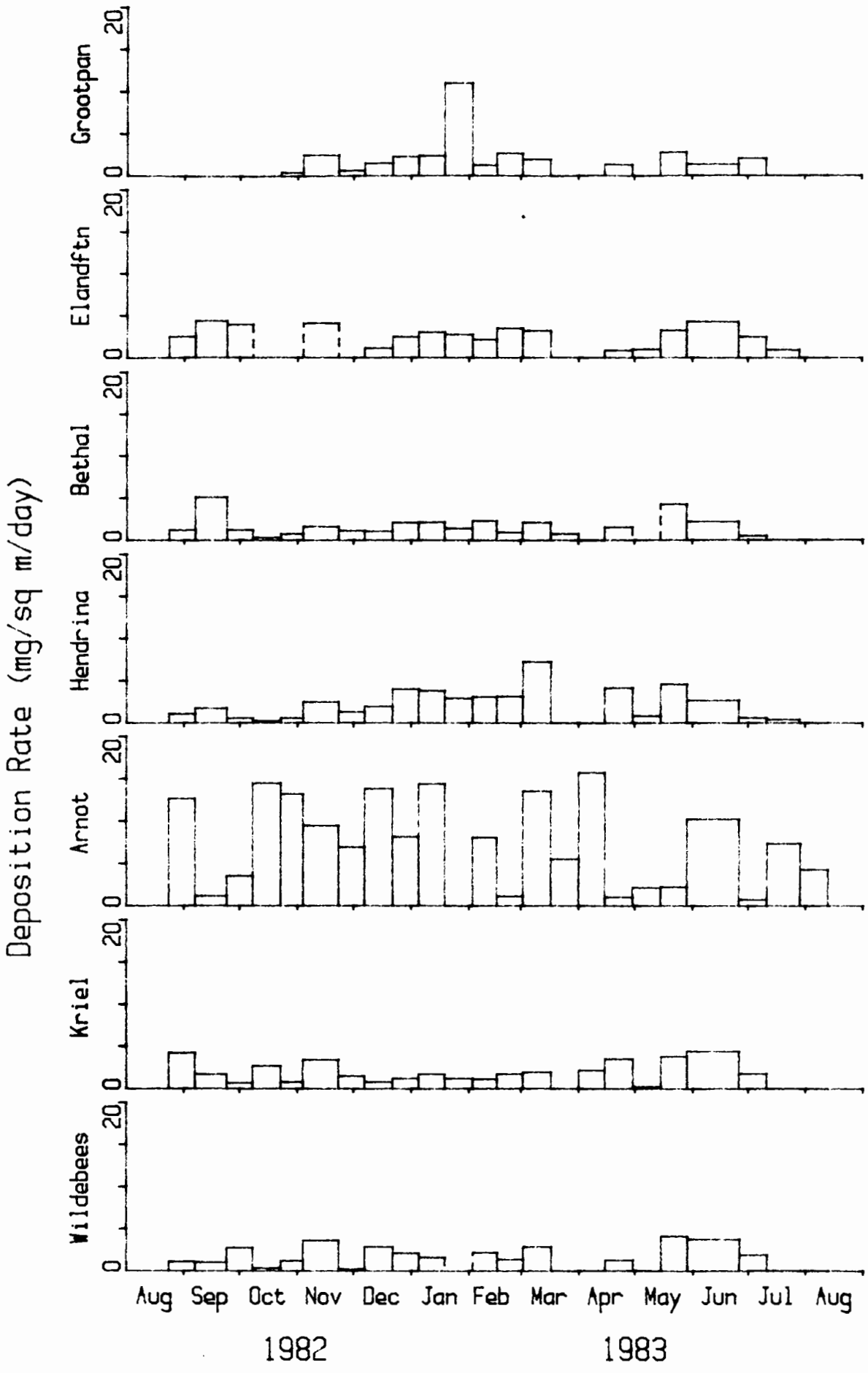


Figure 2.6 : Bulk Deposition rates in mg/sq m/day for Sodium.

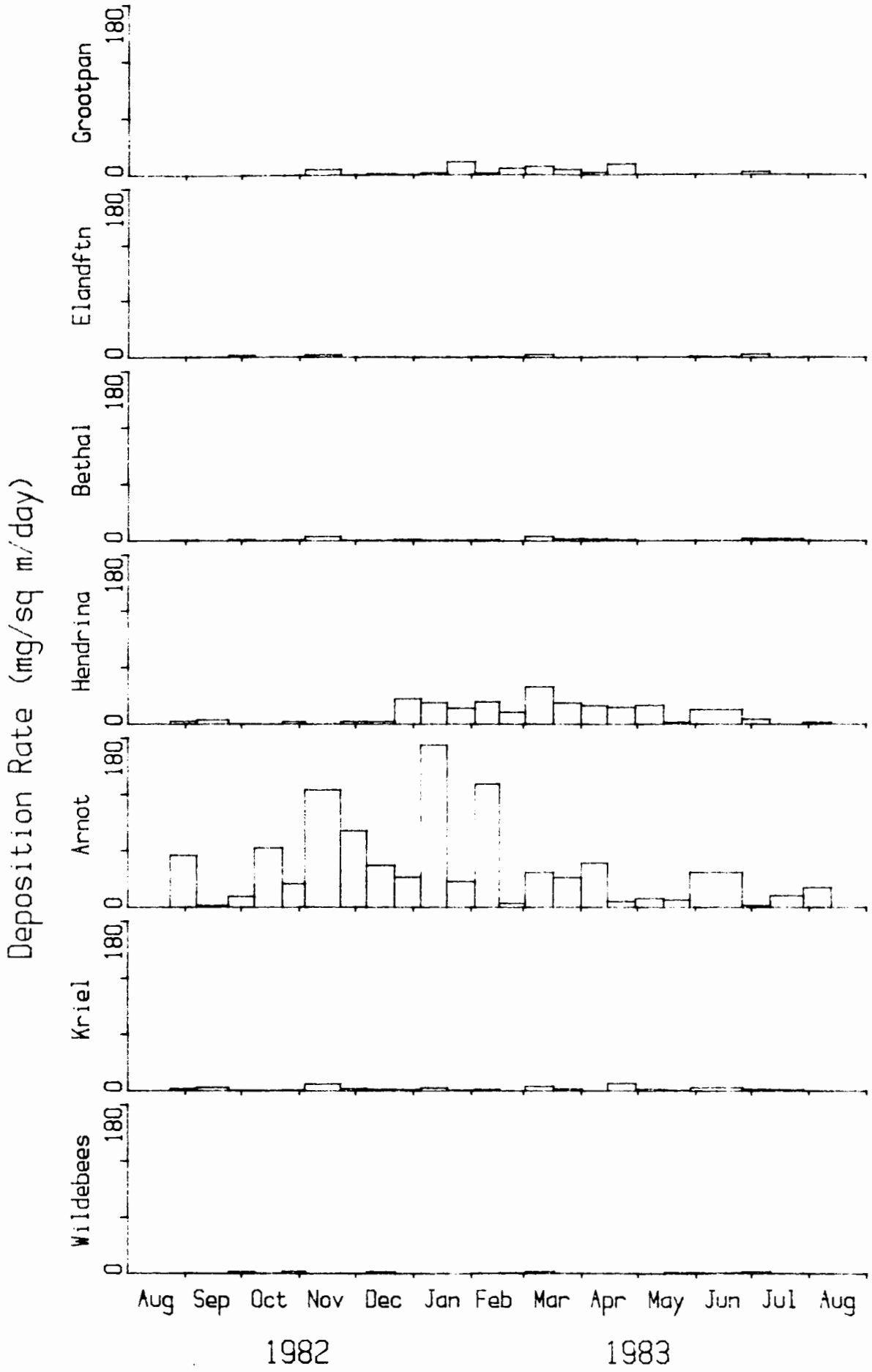


Figure 2.7 : Bulk Deposition rates in mg/sq m/day for Potassium.

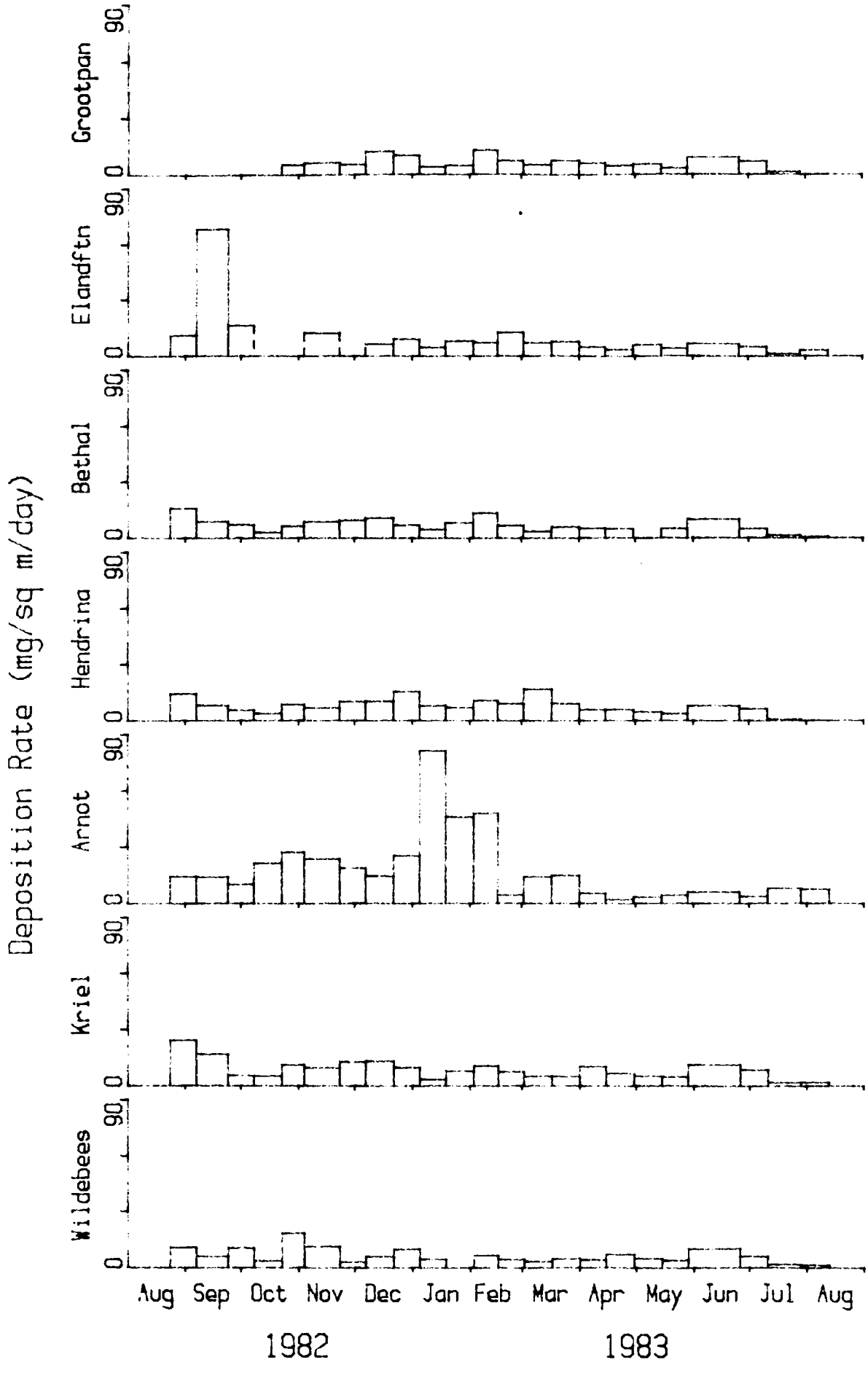


Figure 2.8 : Bulk Deposition rates in mg/sq m/day for Calcium.

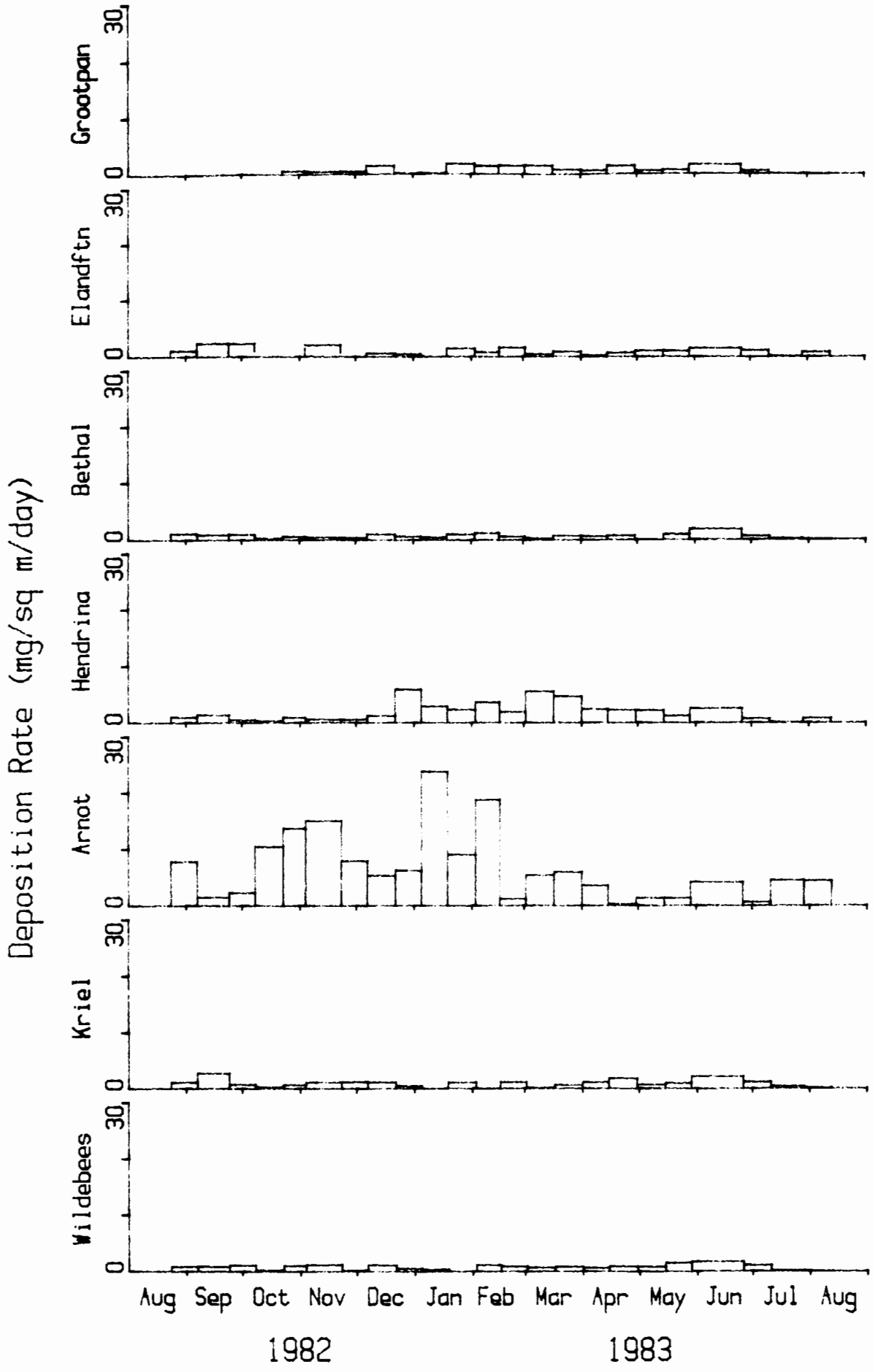


Figure 2.9 : Bulk Deposition rates in mg/sq m/day for Magnesium.

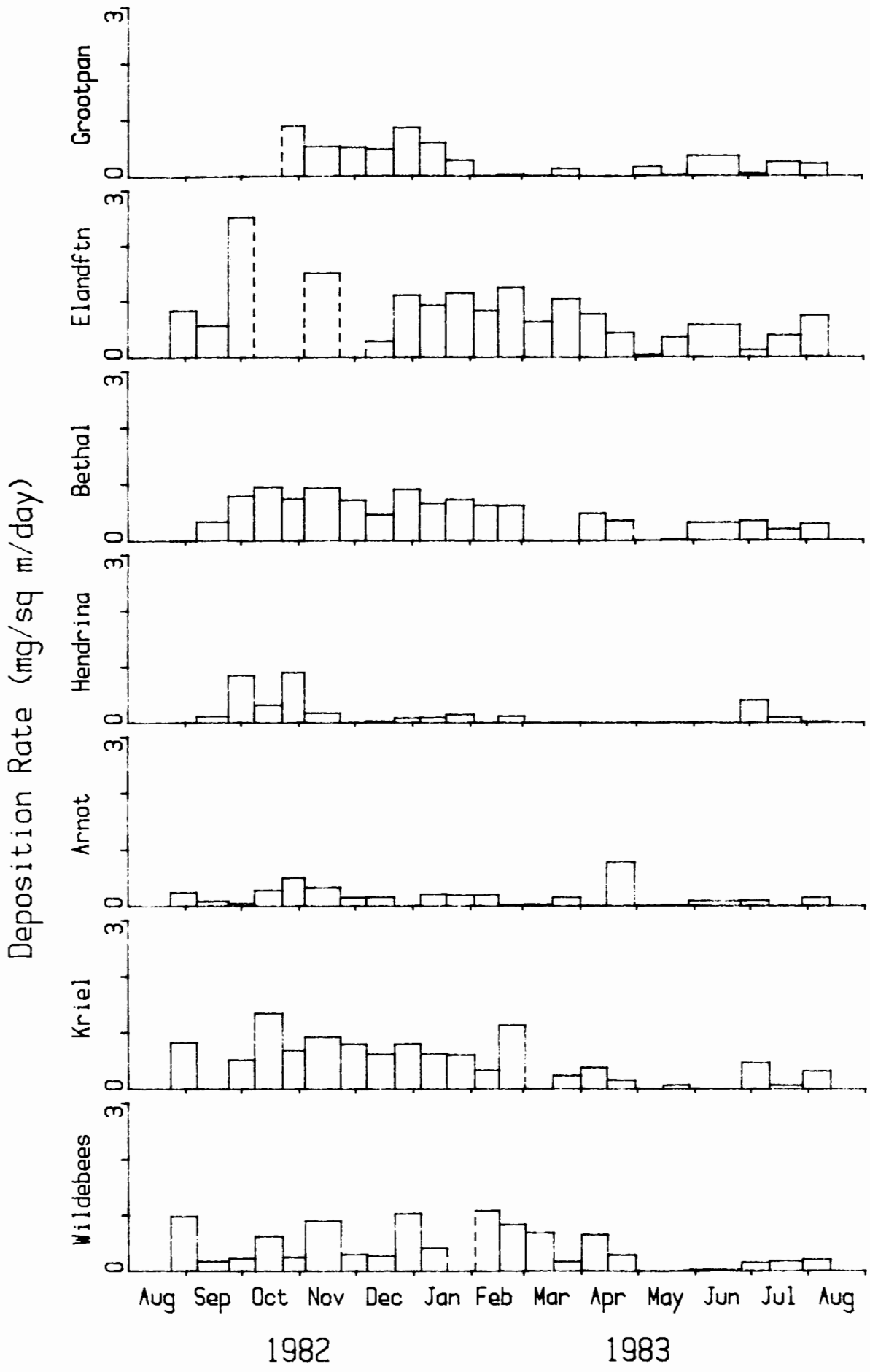


Figure 2.10 : Bulk Deposition rates in mg/sq m/day for Aluminium.

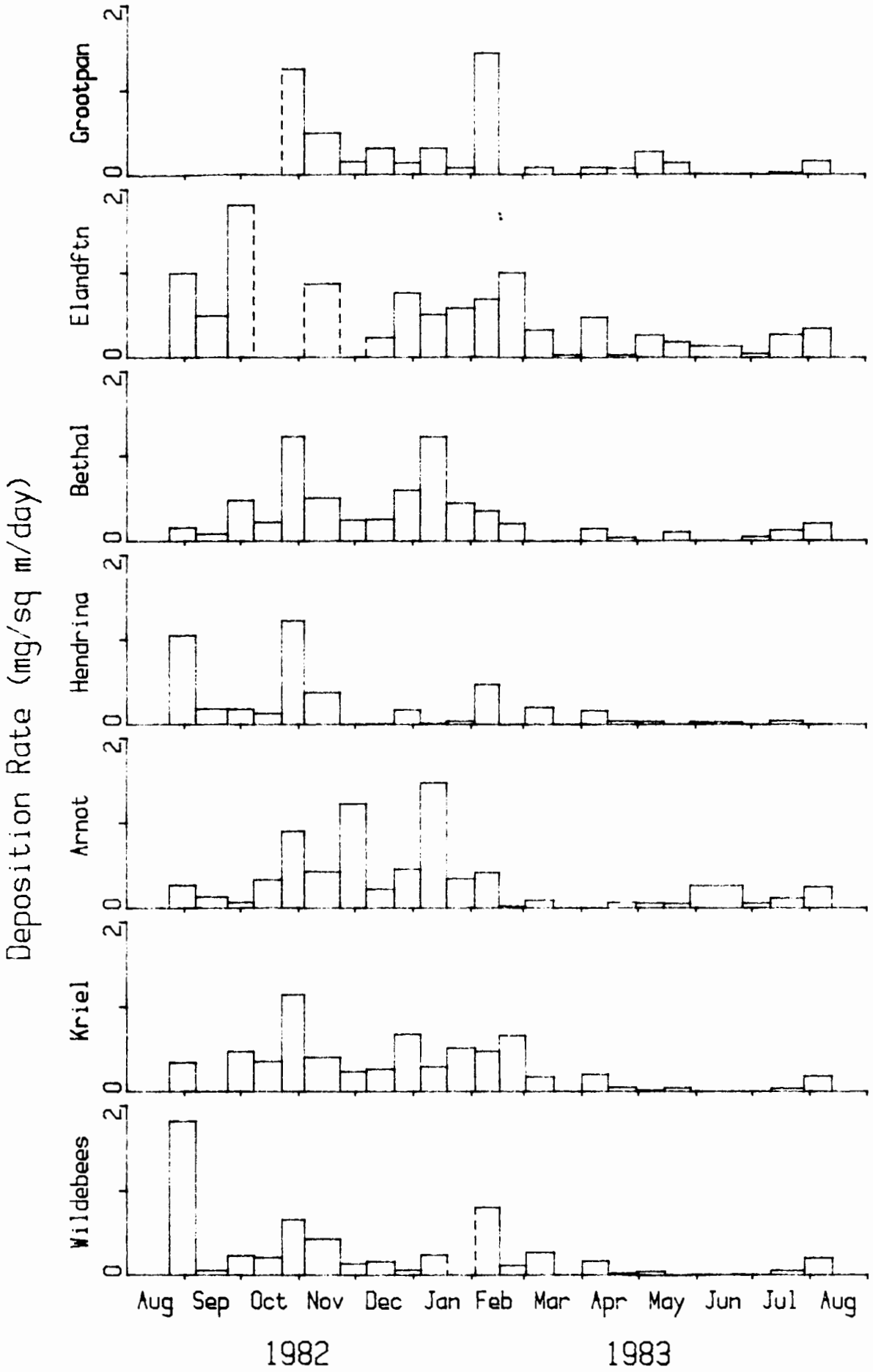


Figure 2.11 : Bulk Deposition rates in mg/sq m/day for Iron.

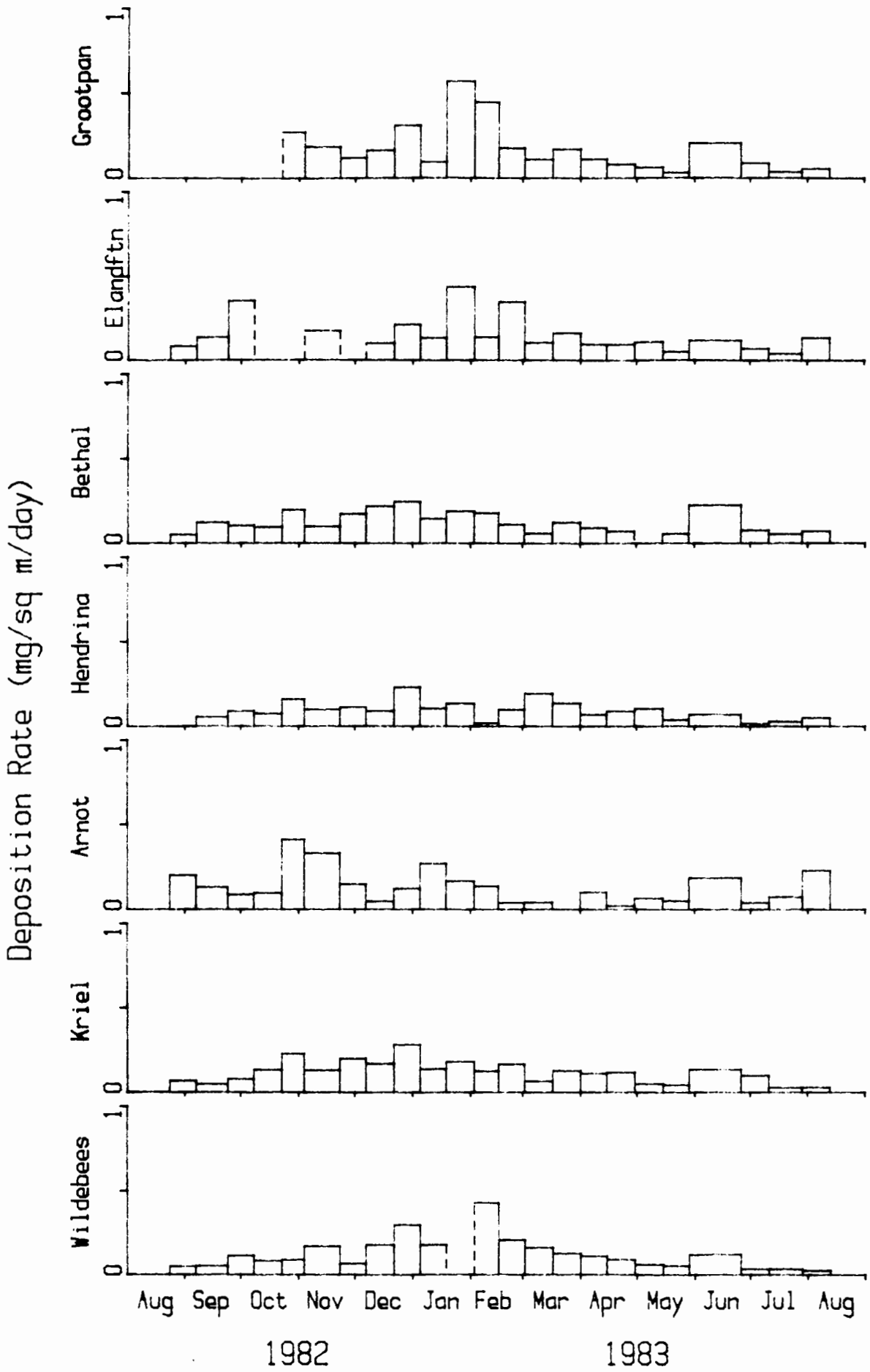


Figure 2.12 : Bulk Deposition rates in mg/sq m/day for Manganese.

APPENDIX 3 : The statistical tables for the bulk deposition data.

Appendix 3.1 : The role of site location and time of year in influencing bulk deposition as determined by 2X2 ANOVA without replications. Significant variations due to these two factors are indicated (***, $p<0.01$; **, $p<0.05$ and ns, not significant).

	Time of year	Spatial Location
Fluoride	**	ns
Chloride	**	***
Nitrate	***	ns
Sulphate	ns	***
Sodium	ns	***
Potassium	ns	***
Calcium	ns	***
Magnesium	ns	***
Aluminium	***	***
Iron	***	ns
Manganese	***	ns

Appendix 3.2 : The range of non-significant differences ($p<0.01$) between the mean bulk depositions recorded at the seven bulk deposition sites, as determined by the Student-Newman-Kuels Test.

Element	Combination
Fluoride	G B H E K A W
Chloride	W B E G H K A
Nitrate	A G H K E B W
Sulphate	B W G K H E A
Sodium	B W K G E H A
Potassium	W E B K G H A
Calcium	W G B E K H A
Magnesium	B W G K E H A
Aluminium	H A G W K B E
Iron	H W G B K A E
Manganese	H E B K W A G

where G : Grootpan site
E : Elandsfontein site
B : Bethal site
H : Hendrina site
A : Arnot site
K : Kriel site
W : Wildebees site

Appendix 3.3 : The range of non-significant differences ($p<0.01$) between the mean daily bulk deposition rates of Fluoride for the exposure periods (as determined by the Student-Newman-Keuls Test), and the season and dominant wind direction for the period.

Exposure Period	Months	Mean Deposition ($mg/m^2/day$)	Season	Dominant Wind Direction
11	Mar	0.00	autumn	N-NW : E-NE
12	Mar/Apr	0.00	autumn	NW-NNW:NNE-NE
13	Apr	0.00	autumn	NW :E
16	Jun	0.00	winter	N-NW
18	Jul	0.00	winter	SW-WNW:ENE
19	Jul/Aug	0.00	winter	SSW:SE:NW
10	Mar	0.03	autumn	E
15	May/Jun	0.04	winter	N-NNW:SW
14	Apr/May	0.09	winter	N-NNW:E
4	Dec	0.09	summer	N-NW
5	Dec/Jan	0.10	summer	N-NW
3	Nov/Dec	0.16	summer	N-NNW
6	Jan	0.23	summer	ENE
9	Feb/Mar	0.24	summer	E
17	Jun/Jul	0.26	winter	NW-WNW:SW:E
2	Nov	0.27	summer	N-NW
8	Feb	0.39	summer	E
7	Jan/Feb	0.50	summer	NE-ENE
1	Oct/Nov	1.75	spring	E

Appendix 3.4 : The range of non-significant differences ($p<0.01$) between the mean daily bulk deposition rates of Nitrate for the exposure periods (as determined by the Student-Newman-Keuls Test), and the season and dominant wind direction for the period.

Exposure Period	Months	Mean Deposition ($mg/m^2/day$)	Season	Dominant Wind Direction
19	Jul/Aug	1.63	winter	SSW:SE:NW
18	Jul	4.48	winter	SW-WNW:ENE
3	Nov/Dec	4.50	summer	N-NNW
15	May/Jun	4.58	winter	N-NNW:SW
14	Apr/May	4.66	winter	N-NNW:E
1	Oct/Nov	6.24	spring	E
16	Jun	7.28	winter	N-NW
10	Mar	7.46	autumn	E
8	Feb	7.84	summer	E
7	Jan/Feb	8.05	summer	NE-ENE
4	Dec	8.13	summer	N-NW
2	Nov	8.56	summer	N-NW
17	Jun/Jul	8.58	winter	NW-NNW:SW:E
13	Apr	8.71	autumn	NW :E
11	Mar	9.99	autumn	N-NW :E-NE
6	Jan	10.90	summer	ENE
9	Feb/Mar	11.60	summer	E
12	Mar/Apr	11.79	autumn	NW-NNW:NNE-NE
5	Dec/Jan	15.01	summer	N-NW

Appendix 3.5 : The range of non-significant differences ($p<0.01$) between the mean daily bulk deposition rates of Aluminium for the exposure periods (as determined by the Student-Newman-Keuls Test), and the season and dominant wind direction for the period.

Exposure Period	Months	Mean Deposition ($mg/m^2/day$)	Season	Dominant Wind Direction
14	Apr/May	0.06	winter	N-NNW:E
15	May/Jun	0.07	winter	NW-NNW:SW
18	Jul	0.17	winter	SW-WNW:ENE
10	Mar	0.19	autumn	E
16	Jun	0.19	winter	N-NW
17	Jun/Jul	0.23	winter	NW-WNW:SW:E
11	Mar	0.25	autumn	N-NW :E-NE
19	Jul/Aug	0.27	winter	SE:SSW:NW
13	Apr	0.28	autumn	NW :E
12	Mar/Apr	0.32	autumn	NW-NNW:NE-NNE
4	Dec	0.33	summer	N-NW
8	Feb	0.44	summer	E
3	Nov/Dec	0.48	summer	N-NNW
6	Jan	0.50	summer	ENE
7	Jan/Feb	0.55	summer	NE-ENE
9	Feb/Mar	0.57	summer	E
5	Dec/Jan	0.68	summer	N-NW
1	Oct/Nov	0.70	spring	E
2	Nov	0.75	summer	N-NW

Appendix 3.6 : The range of non-significant differences ($p<0.01$) between the mean daily bulk deposition rates of Iron for the exposure periods (as determined by the Student-Newman-Keuls Test), and the season and dominant wind direction for the period.

Exposure Period	Months	Mean Deposition ($mg/m^2/day$)	Season	Dominant Wind Direction
11	Mar	0.01	autumn	N-NW : E-NE
17	Jun/Jul	0.02	winter	NW-NNW:SW:E
13	Apr	0.04	autumn	NW :E
16	Jun	0.06	winter	N-NW
15	May/Jun	0.07	winter	N-NNW:SW
18	Jul	0.09	winter	SW-WNW:ENE
14	Apr/May	0.11	autumn	N-NNW:E
10	Mar	0.16	autumn	E
12	Mar/Apr	0.17	autumn	NW-NNW:NE-NNE
19	Jul/Aug	0.19	winter	NW:SSW:SE
4	Dec	0.21	summer	N-NW
9	Feb/Mar	0.29	summer	E
7	Jan/Feb	0.36	summer	NE-ENE
3	Nov/Dec	0.36	summer	N-NNW
5	Dec/Jan	0.41	summer	N-NW
2	Nov	0.50	summer	N-NW
6	Jan	0.58	summer	ENE
8	Feb	0.66	summer	E
1	Oct/Nov	1.07	spring	E

Appendix 3.7 : The range of non-significant differences ($p<0.01$) between the mean daily bulk deposition rates of Manganese for the exposure periods (as determined by the Student-Newman-Keuls Test), and the season and dominant wind direction for the period.

Exposure Period	Months	Mean Deposition ($mg/m^2/day$)	Season	Dominant Wind Direction
18	Jul	0.04	winter	SW-WNW:ENE
15	May/Jun	0.05	winter	N-NNW:SW
17	Jun/Jul	0.06	winter	NW-WNW:SW:E
14	Apr/May	0.07	winter	N-NNW:E
13	Apr	0.08	autumn	NW :E
19	Jul/Aug	0.08	winter	SSW:SE:NW
12	Mar/Apr	0.10	autumn	NW-NNW:NE-NNE
10	Mar	0.10	autumn	E
11	Mar	0.12	autumn	N-NW :NE-E
3	Nov/Dec	0.14	summer	N-NNW
4	Dec	0.14	summer	N-NW
16	Jun	0.15	winter	N-NNW
6	Jan	0.15	summer	ENE
9	Feb/Mar	0.16	summer	E
2	Nov	0.17	summer	N-NW
8	Feb	0.21	summer	E
1	Oct/Nov	0.22	spring	E
5	Dec/Jan	0.24	summer	N-NW
7	Jan/Feb	0.28	summer	NE-ENE

APPENDIX 4 : The statistical tables for the wet deposition data.

Appendix 4.1 : The role of site location in influencing the concentrations (μeq/l) and loadings (μeq/m^2) of wet depositions as determined by 1X1 ANOVAs without replications. Significant variations due to these two factors are indicated (***, $p<0.01$; **, $p<0.05$ and ns, not significant).

	Spatial Location (μeq/l)	Spatial Location (μeq/m^2)
Hydrogen ions	ns	ns
Fluoride	ns	ns
Acetate	ns	ns
Formate	ns	ns
Chloride	ns	***
Nitrate	ns	ns
Sulphate	ns	ns
Sodium	ns	ns
Ammonium ions	ns	ns
Potassium	ns	ns
Calcium	***	***
Magnesium	ns	ns
Aluminium	ns	ns
Iron	ns	ns
Manganese	ns	ns

Appendix 4.2 : The role of site location and time of year in influencing the wet deposition loadings ($\mu eq/m^2$) for the seven wet periods, as determined by 2X2 ANOVAs without replications. The wet periods are defined as those periods when at least three of the four sites sampled rain.
Significant variations in deposition due to the period and spatial location of the site are indicated (***, $p<0.01$; **, $p<0.05$; and ns, not significant).

	Time of year	Spatial Location
Hydrogen ions	***	ns
Fluoride	ns	ns
Acetate	ns	ns
Formate	ns	ns
Chloride	ns	ns
Nitrate	**	ns
Sulphate	***	ns
Sodium	ns	ns
Ammonium ions	**	ns
Potassium	ns	ns
Calcium	ns	ns
Magnesium	***	ns
Aluminium	ns	ns
Iron	ns	ns
Manganese	ns	ns

Appendix 4.3 : The range of non-significant differences ($p<0.01$) between the mean wet depositions (mg/m^2) recorded during seven wet periods (Student-Newman-Keuls Test). The ranges for nitrate and ammonium ions are at the $p<0.05$ level. A wet period was defined when at least three of the four sites sampled rain.

Element	Combination
Hydrogen ions	7 2 6 1 3 5 4
Fluoride	5 6 2 7 4 3 1
Acetate	5 6 3 4
Formate	5 6 3 4 1
Chloride	5 2 7 6 3 1 4
Nitrate	7 2 6 5 1 3 4
Sulphate	7 2 1 6 3 5 4
Sodium	5 2 7 6 1 4 3
Ammonium ions	7 2 5 6 3 1 4
Potassium	1 5 2 4 7 3 6
Calcium	7 4 5 2 6 3 1
Magnesium	7 5 1 6 2 3 4
Aluminium	6 5 2 7 1 3 4
Iron	5 2 6 4 1 7 3
Manganese	6 5 4 1 2 7 3

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